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Supercritical Fluid Processing
of Propellant Polymers

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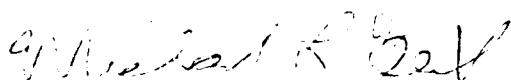
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Polymeric pre-propellant binders are known to be heterogeneous materials exhibiting significant variation with respect to molecular weight, structure, functionality, and related performance properties. The objective of this program was to demonstrate the feasibility of fractionating propellant binders with supercritical fluid (SCF) solvents. Hydroxy-terminated polybutadiene (HTPB) (R-45M, Atochem North America) was fractionated with supercritical propane yielding ten fractions with number average molecular weights ranging from 780 to 11760 and polydispersities of approximately 1.2. The increase in hydroxyl equivalent weight with molecular weight was found to be nonlinear, with functionality increasing rapidly in the higher molecular weight fractions. Non-functional cyclic and other low molecular weight components were effectively extracted from glycidyl azide polymer (GAP) using supercritical carbon dioxide as evidenced by HPLC analysis. GAP was fractionated across the entire molecular weight distribution using HCFC-22. Extraction of the GAP precursor, polyepichlorohydrin (PECH), was also investigated. Several other aspects of SCF extraction were

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19. ABSTRACT cont.

investigated including choice of solvent and process parameters, the effect of extraction on free water content, and the use of liquified gases for low pressure stripping of the polymers.

The molecular weight dependence of the physical properties, which ultimately influence the performance properties of the binders, suggests that each fraction will exhibit cure and combustion properties different from each other and from the parent material. SCF extraction may be readily scaled to produce large quantities of fractionated binder for performance tests and field evaluation.

EXECUTIVE SUMMARY

Polymeric pre-propellant binders are known to be heterogeneous materials exhibiting significant variation with respect to molecular weight, structure, functionality, and related performance properties. The objective of this program was to demonstrate the feasibility of fractionating propellant binders with supercritical fluid (SCF) solvents.

Two candidate materials, hydroxy-terminated polybutadiene (HTPB) and glycidyl azide polymer (GAP) were selected by the Astronautics Lab for evaluation. Both materials exhibit molecular weight dependent performance properties and are thought to contain fractions within the parent distribution and impurities which are responsible for performance problems. The precursor to GAP, polyepichlorohydrin (PECH), was also evaluated. Several solvents including propane, carbon dioxide, and HCFC-22 were used. The significant findings regarding fractionation are summarized below.

HTPB was fractionated with propane yielding ten fractions with number average molecular weights ranging from 780 to 11760 and polydispersities of about 1.2. The increase in hydroxyl equivalent weight with molecular weight was found to be non-linear with functionality increasing rapidly in the higher molecular weight fractions.

Non-functional cyclic and other low molecular weight components were effectively extracted from GAP using carbon dioxide as evidenced by HPLC analysis. GAP was fractionated across the entire molecular weight distribution using HCFC-22.

Several other aspects of SCF extraction were investigated including choice of solvent and process parameters, the effect of extraction on free water content, and the use of liquified gases for low pressure stripping of the polymers.

There are three primary motives for fractionating HTPB and GAP and each requires processing on a different scale. As an analytical tool, analysis of small fractionated samples can elucidate the molecular weight dependence of critical properties such as functionality. Additionally, the feasibility of removing other interfering species may be determined. The second motive which requires a somewhat larger scale fractionation is to generate samples for performance testing. The results of these tests would provide definitive data regarding identification of the optimal and deleterious fractions for use in propellant casting. The final motive is to provide a source of pre-propellant binder with consistent and optimum properties. Lot to lot variation could be minimized or eliminated by isolating only the optimum fraction(s) from each batch and using the balance for less critical applications, e.g., urethane elastomers or coatings for HTPB.

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I. INTRODUCTION - Identification of the Problem

The problem, Separation and Purification of Propellant Polymers, AF-193, FY 90 DOD SBIR, was well described in the topic solicitation: certain rocket motor failures can be traced to presence of low molecular weight contaminants in binder polymers. Varying amounts of low molecular weight materials present in propellant binders, especially those species containing no reactive functionality and thus not incorporated chemically into block or crosslinked polymer systems, can interfere with the performance of rocket motors. Additional problems arise because of the polydisperse nature of polymeric binders. Since many performance properties are related to molecular weight, e.g., functionality, viscosity and volatility, the heterogeneous nature of these polymers result in significant variations in the cure and combustion properties of the propellants and hence the engines themselves. Additionally the functionality of some of the polymer chains (e.g. hydroxy-terminated polybutadiene) is not consistent with molecular weight and therefore can cause nonuniformities in the reacted matrix. This problem is compounded by the significant lot to lot variation often observed in binder polymers. As an example Carver (1) has recounted the multi-million dollar costs associated with the re-evaluation of several thousand HAWK motors necessitated by variation encountered in amounts of insoluble material present in the polymeric neopentyl glycol azelate (NPGA) binder.

Laub (2) summarizes (from Refs 3 & 4) the various polymeric binders used in composite propellant formulations for DOD missile systems, e.g., these include: polyneopentyl glycol azelate (NPGA) in HAWK; hydroxy-terminated polybutadiene (HTPB) in VIPER, PATRIOT, MET ROCKET GSRS, PERSHING, and HELLFIRE; polybutadiene acrylic acid (PBAA) in PERSHING and SPARTAN systems. Composite smokeless propellants containing polyethylene glycol (PEG), polyethylene glycol adepate (PEGA) and polycaprolactone are currently under development. Glycidyl azide polymer (GAP) is under evaluation as an energetic, smokeless propellant. All of these binders, because of their polymeric nature exhibit to a greater or lesser extent, the problems arising from inhomogeneity and lot to lot variation mentioned above.

Over the years, millions and millions of dollars have been spent by DOD on prepropellant polymer characterization (refs Laub (2), Stephen Campbell and Webb (5), etc.). Most of these studies have been directed towards establishing a dependence of performance properties on the physical properties of the binder such as molecular weight, functionality, presence of insoluble materials, etc. In many cases these studies involved analytical scale fractionation to determine the distribution and composition of the polymer. Several theories have been developed as to the favorable and deleterious properties of each binder and the characterization used as a quality control mechanism to determine which lots of polymer would perform well in a composite propellant system. Unfortunately none of the analytical fractionation techniques can realistically be scaled up to produce fractions large enough in size to carry out performance evaluation to generate hard data regarding the molecular weight dependence of performance properties.

The majority (if not all) of rocket propellant polymers exhibit characteristics that prevent their being processed for performance enhancement by current standard industrial separations technology to remove interfering species. For example, distillation (even under high vacuum) or solvent extraction is not effective; in the case of distillation, the interfering species exhibit such a low vapor pressure that they cannot be separated, and in the case of solvent extraction, no single solvent can be tuned so as to differentiate between the desired and undesired components or species of differing molecular weight. The topic solicitation recognized the limitations of current

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conventional technology when it sought proposals to apply supercritical fluid extraction as a potentially viable and scaleable technique for the removal of low molecular weight species and unreacted raw materials.

Liquid solvent extraction can, at the analytical or small preparative scale, separate or fractionate by undesired/desired components or by molecular weight progression, but, in general, it is not readily practicable at a production level. It is of pedagogical value to describe how liquid solvent extraction (or partitioning) is practiced on an analytical scale, specifically as applied to the fractionation of hydroxyterminated polybutadiene. and to present some laboratory data of Laub (2). Two variations of solvent fractionation are, in principle, possible: in the first, called fractional precipitation, the composition of a binary solvent is adjusted in a step-gradient manner so as to yield successively-insoluble fractions of polymer. Since solubility is presumed to be a function of molecular weight (MW), the precipitated fractions obtained are in order of decreasing MW. An alternative and entirely equivalent method comprises fractional solution wherein a neat sample is extracted into solvent mixtures of increasing solubilization strength, decreasing "polarity", since lower molecular-weight homologs of species such as HTPB are more soluble in more "polar" solvents. As above, solubility of the prepolymer is a function of MW; the fractions in the fractional solution are in this variant, in order of increasing molecular weight. The latter technique has proved over the years to be more convenient in the instance of crystalline polymers, since fractions are taken up in solution (thence removed) as opposed to requiring isolation by filtration.

For fractionating HTPB (R-45M) Laub (2), Ramey (3), and Blanks, Shephard, and Stephens (4) used a solvent composed of isopropyl alcohol (IPA) and benzene. As stated, fractional solution fractionation employs a polarity gradient elution program in which incremental amounts of benzene are added to IPA that is initially passed through a column containing HTPB to elute first the fraction of low molecular weight and most polar species; species are eluted (extracted) in order or decreasing solubility in the mobile phase (the extractant solvent) and the most-soluble solutes elute (are extracted) first. Further, and in order that homologs be eluted at roughly constant intervals, a gradient elution program can be used to alter the solvent polarity during a run (similar to temperature-programming in gas chromatography) while, in the case of discontinuous batch-wise solvent extraction, the analogous technique is the changing of the composition of the extractant liquid stepwise.

Several interesting features were immediately apparent from the results obtained for the analytical-scale solvent fractionation utilizing IPA + benzene (35°C) [as recommended by Ramey (2), and by Blanks, Shephard, and Stephens (3)]. First, the total amount obtained for Fraction 1 was very large, and comprised very nearly 15% (w/w) of the total sample. Laub hypothesized that this might be a result of the extraction of water, peroxides, and stabilizers. Also, there was a step-like decrease of the amounts obtained of each fraction on passing from IPA extractant through ~15% v/v benzene in IPA. Thereafter, the amounts obtained increased as the amount of benzene in the extractant solvent was increased until, at 40% benzene, nearly 20% of the total weight of R-45M was removed (Fraction 9). The next fraction, #10, was that obtained with 50% benzene, in which all of the remaining R-45M was soluble. The molecular weight analysis of the fractions is given in Table 1.

TABLE 1

Fractionation Results from Laub (2) Gradient Elution with IPA and Benzene

Fraction No.	M/Da*	% wt/wt
1A**	1,440	7.49
1B	1,620	5.08
1C	1,785	2.97
2A	2,050	2.46
2B	2,355	2.08
2C	2,500	1.83
3A	2,600	1.90
3B	2,550	1.88
3C	2,645	1.71
4A	3,045	1.95
4B	3,180	2.04
4C	3,345	1.98
5A	3,665	2.27
5B	3,575	2.45
5C	3,645	2.37
6A	4,045	2.99
6B	4,110	3.39
6C	4,560	3.35
7A	4,745	3.83
7B	5,205	4.22
7C	5,360	3.82
8A	6,415	5.33
8B	7,430	5.67
8C	8,505	4.82
9A	10,230	7.66
9B	11,630	7.17
9C	13,010	3.15
10A	28,355	4.14

* Peak maximum molecular weight
** Fractions were collected in three "sub fractions" (except for 10)

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Most of the fractions were obtained after standing for 18 h; however, some were allowed to remain quiescent for 1 1/2 days for phase separation. No trends in the relative amounts obtained could be discerned, that is, the amounts recovered appeared to reach a constant value after 18 h. In a repeat of this work, Laub allowed each fraction to sit for at least 1 week for phase separation, but the results differed little from those found in which 18-h standing times were used. As shown in Table I the process can effectively separate components by molecular weight, but one disadvantage of fractional solution fractionation (using liquid solvents) resides in the long time, distillation, or drying, etc. required for separation of liquid solvent from the polymer.

II. Principles of Supercritical Fluid Extraction

A. Background on Supercritical Fluid Solubility

The phenomenon of solubility in supercritical fluids has been well covered in the literature, in symposia proceedings (6,7) in books (8,9) and in many journals (e.g., 10, 11, 12), but a brief background is presented here primarily for purposes of completeness in a document that may be issued as a technical report in the future. These articles have described the advantages of supercritical fluid extraction in a broad range of applications, such as coffee decaffeination, spice extraction, and lipids purification. The processing principles have also long been well known and practiced in the polymer industry, especially in the operation of the high pressure polyethylene process which was developed in the late 1930s (6), and Phasex Corporation has identified polymers processing as an ideal application of the properties of supercritical fluids (13).

A gas or liquid at ambient conditions becomes a supercritical fluid (SCF) when it is compressed and heated to conditions of temperature and pressure above its critical point. In the critical region a gas exhibits a liquidlike density and a much increased solvent capacity that is pressure-dependent. The variable solvent capacity of a supercritical fluid is the basis on which separations processes can be devised, and it was these properties which led the topic sponsor to propose the application of supercritical fluids for selectively extracting certain components from propellant binders.

The critical temperatures of gases and liquids can differ by hundreds of degrees, and this difference suggests the use of specific supercritical fluids in specific applications. For example, because the critical temperatures of carbon dioxide, ethane, and ethylene are near ambient, they are attractive solvents for processing heat-sensitive flavors, pharmaceuticals, labile lipids, and reactive monomers and macromonomers. Substances that are less temperature-sensitive, such as most industrial chemicals and polymers, are readily treated with the C-3 and C-4 hydrocarbons with critical temperatures in the range of $100\text{-}150^\circ C$; the C-3 and C-4 hydrocarbons are generally better solvent for polymers than the C-2 hydrocarbons.

In historical development of supercritical fluid solubility, Hannay and Hogarth (14) are credited as the first investigators to examine the unique solvent properties of supercritical fluids. They found that certain alkali halide salts remained dissolved in ethanol when the temperature and pressure were raised to conditions above the critical point of the solution. They found, furthermore, that in the region near the critical point, pressure alone could be used to control the solubility of the salts. When the system pressure was lowered isothermally, the dissolved salt precipitated from solution, and when the pressure was raised isothermally, the precipitated salt redissolved. At the end of their paper Hannay and Hogarth wrote: "We have, then, the phenomenon of a solid with no measurable vapor pressure, dissolving in a gas... When the solid is precipitated by suddenly reducing the pressure, ... it may be brought down as a 'snow' in the gas...." Based on these now more than 100-year-old findings, separations processes using the pressure-dependent dissolving power of supercritical fluids are being developed.

Knowledge of the solubility behavior of a material in a supercritical fluid is important in assessing the processing potential of these solvents. Figure 1 shows the solubility behavior of one compound, naphthalene, in two gases, ethylene and carbon dioxide. At low pressures (< 1-2 MPa or 10-20 bar) the solubility of naphthalene in both gases is low, as might be expected, and
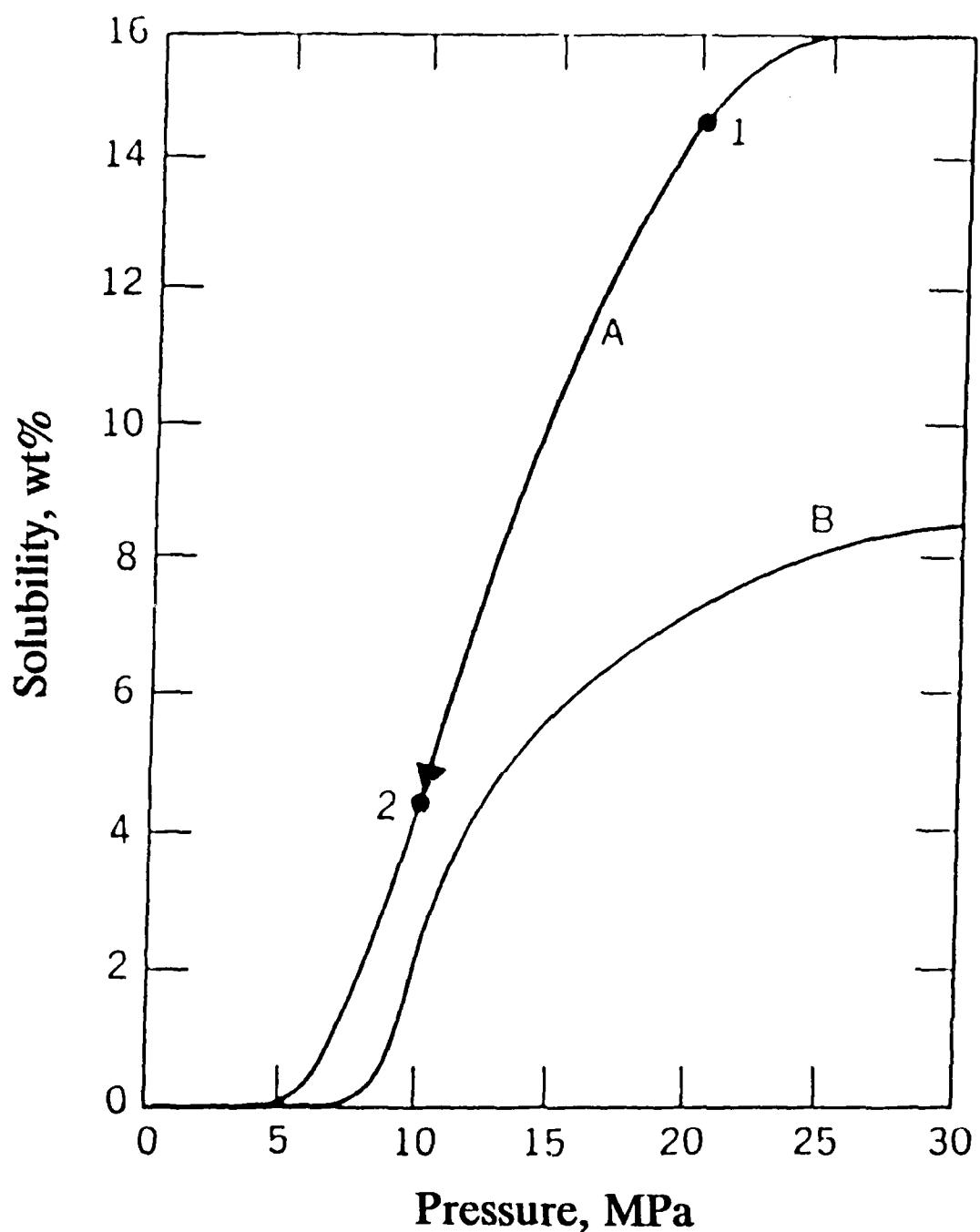
Figure 1. Solubility of Naphthalene in Ethylene, 35°C (A) and Carbon Dioxide, 45°C (B)

is readily calculable from solely vapor pressure considerations. As the pressure is increased and as the critical pressure of each gas is approached, the solubility begins to increase rapidly, and as the pressure is raised still further, the solubility of naphthalene rises dramatically to high levels. The rapid rise in solubility occurs at about the critical pressure of each gas (5.04 MPa or 50.4 bar for ethylene and 7.38 MPa or 73.8 bar for carbon dioxide).

The solubility behavior depicted in Figure 1 is, to a first approximation, attributable to changes in the gas der· ty. As the critical pressure is approached, the density of a gas increases rapidly, and at high density conditions the solvent power is greatly increased because of increased intramolecular forces related to molecule-molecule proximity considerations. Numerous authors have shown that this increase in solubility is not merely the result of a hydrostatic pressure effect on the solid, i.e., a raising of its vapor pressure. Instead, the rise in solubility near the critical point is a result of increased dispersion forces operating in dense gases. This behavior can frequently be calculated accurately with a simple cubic equation of state (15), which accounts for interactions of the specific solvents and solutes; other factors such as acid-base complexing and hydrogen bonding can also be operative in the critical region (16). For example, carbon dioxide although strictly a non polar molecule, has a strong quadrapole moment that gives it the ability to solvate polar compounds such as methanol.

Figure 1 shows that at pressures higher than the respective critical pressures the solubility of naphthalene is higher in ethylene than in carbon dioxide. A priori it might be anticipated that naphthalene (and other solutes) would dissolve to different concentrations in the two gases, just as it would be anticipated that, for example, polymers would dissolve to different extents in different liquid organic solvents. As discussed later, polymers also dissolve to different extents in different supercritical fluids.

The solubility behavior shown in Figure 1 is general and is exhibited by any liquid or solid material that dissolves in a supercritical fluid, and this general solubility behavior can be exploited in separations processes. For example, using the pressure-dependent dissolving power of a supercritical fluid, a compound can be dissolved, extracted, or purified. A specific illustration is the condition at Point 1 (~20 MPa or 200 bar, 35°C) on the naphthalene-ethylene solubility curve in Figure 1. Naphthalene can be dissolved in ethylene at this condition and extracted from some other insoluble (or slightly soluble) compounds. Isothermally lowering the pressure to Point 2 (~10 MPa or 100 bar, 35°C) greatly reduces naphthalene solubility, resulting in precipitation from the ethylene solution; it drops out as a "snow". The naphthalene snow can be collected in a suitable separator vessel, and the ethylene can be recompressed and delivered to the extractor vessel to continue the extraction-separation cycle. A generic extraction process using the pressure-dependent solvent properties of supercritical fluid solvents was explicitly described by Todd and Elgin in 1955 (17), and a description of the process operation is given below.

B. Supercritical Fluid Extraction Process Operation

There are many operations that can be carried out with supercritical fluids. For its simplicity a batch extraction of solid materials is described first.

1. Batch Extraction of Solid Materials

A schematic diagram of the extraction process described by Todd and Elgin is shown in Figure 2. Four major pieces of equipment are shown in the figure, viz., an extraction vessel, a pressure-reduction valve, a separator, and a compressor. (For simplicity and ease of discussion, ancillary pieces of equipment, such as gauges, controls, facilities for storing gas, etc., are not shown in the figure). The solubility behavior of naphthalene-CO_2 is also shown in Figure 2 as a function of temperature and pressure; solubility isobars from 70 to 300 atm are given. Several directed lines, e.g., line segment 1-2, 1-3, are also given in the figure and the end points of the segments represent extraction and solute separation conditions.

To illustrate the operation of the process, assume that the extractor has been filled with a 50/50 mixture of naphthalene and some insoluble material, e.g., powdered chalk. Chalk, Calcium/Magnesium Carbonate, does not dissolve in carbon dioxide. Incidentally, the filling of the vessel with the solid mixture, although "an engineering detail" for this discussion, is not necessarily an easy task and is, furthermore, not without substantial capital and operating costs in the overall separation process. The mixture is probably not continuously "pumpable" into the extraction vessel during high-pressure operation; it instead will probably be charged in a batch mode through quick-acting gate valves or through some other motor-activated opening. Because the filling and extraction operations are done in a batch mode, it might be desirable to have two or three extraction vessels in parallel, and these concepts are easily extrapolated to a multivessel system with different substances and different gas solvents.

Once the naphthalene-chalk dust mixture is charged to the vessel and the vessel scaled, carbon dioxide is compressed and heated to the desired operating conditions. When the pressure reaches the desired operating level, the pressure-reduction valve is actuated and CO_2 flow commences. Using the data in Figure 2 operation with extraction conditions at 300 atm and 55°C will be described. As carbon dioxide flows through the vessel, naphthalene dissolves in the stream of CO_2 to a concentration level of 15 wt-% (see point 1 in Figure 2). The loaded CO_2 phase leaving the extractor is expanded, for purposes of illustration, to 90 atm through the pressure-reduction valve. When the pressure is lowered, naphthalene precipitates from solution. An isenthalpic (i.e., constant-enthalpy) expansion of the carbon dioxide-rich stream, causes a drop in temperature of about 19°C (as calculated from thermodynamic data for pure carbon dioxide), and, thus, the expansion path on the naphthalene solubility diagram is shown as an oblique line. At 90 atm and 36°C the equilibrium solubility of naphthalene in CO_2 is only 2.5 wt-%. The naphthalene that has precipitated is collected in the separator, and the carbon dioxide stream is recompressed to the initial extraction conditions of 55°C and 300 atm and is recycled to the extractor.

It is informative to follow the process cycle on a carbon dioxide Mollier diagram for the purpose of determining the energy requirements of this SCF process relative to some other process for separating the two materials and the extraction will be compared to the vaporization of the naphthalene at its boiling point (218°C). An enlarged view of the pertinent section of the temperature-entropy diagram of carbon dioxide is given in Figure 3. The arrows on this figure trace the path of CO_2 in the process cycle. As previously described, the extraction step occurs at 55°C and 300 atm (point 1 in Figure 3). The CO_2-naphthalene solution leaving the extractor is isenthalpically expanded across the pressure-reduction valve to 90 atm (to point 2). During the expansion step, the temperature of the CO_2 solution falls about 19°C (the heat effects associated

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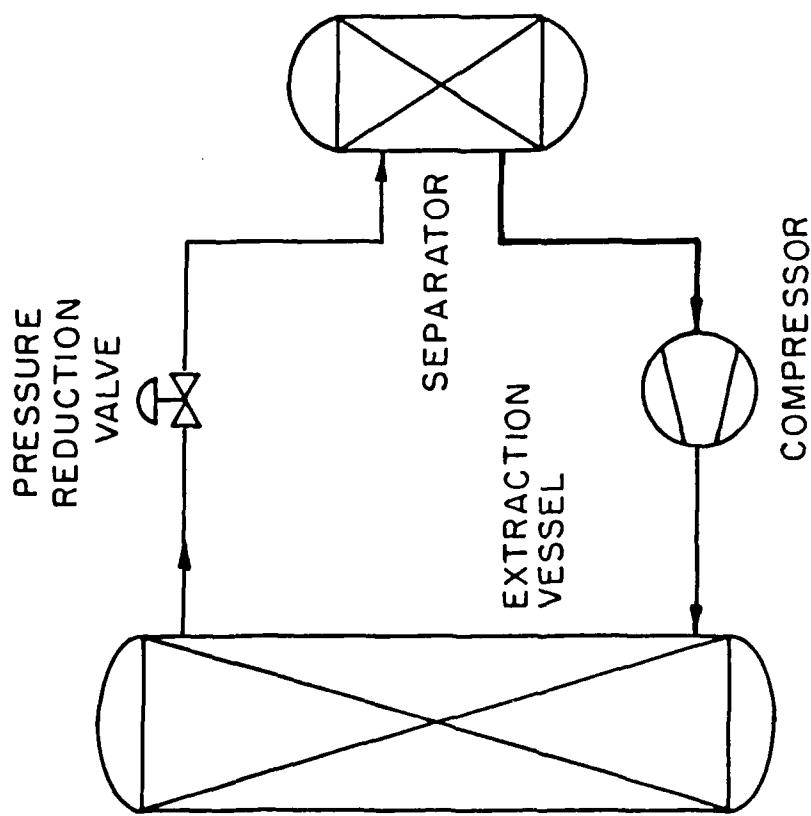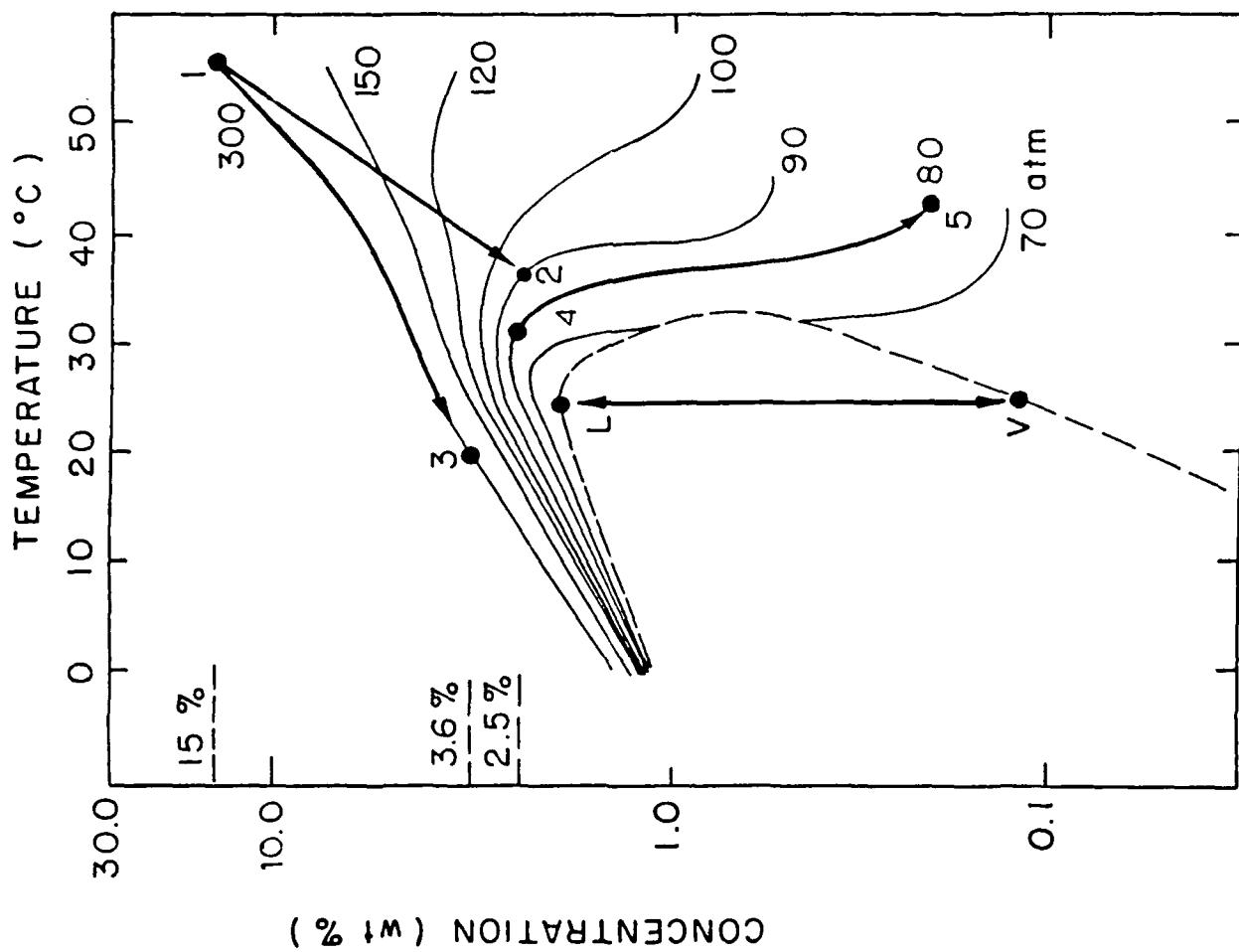
Figure 2. Extraction Process Operation (Using Naphthalene Solubility Behavior in CO_2)

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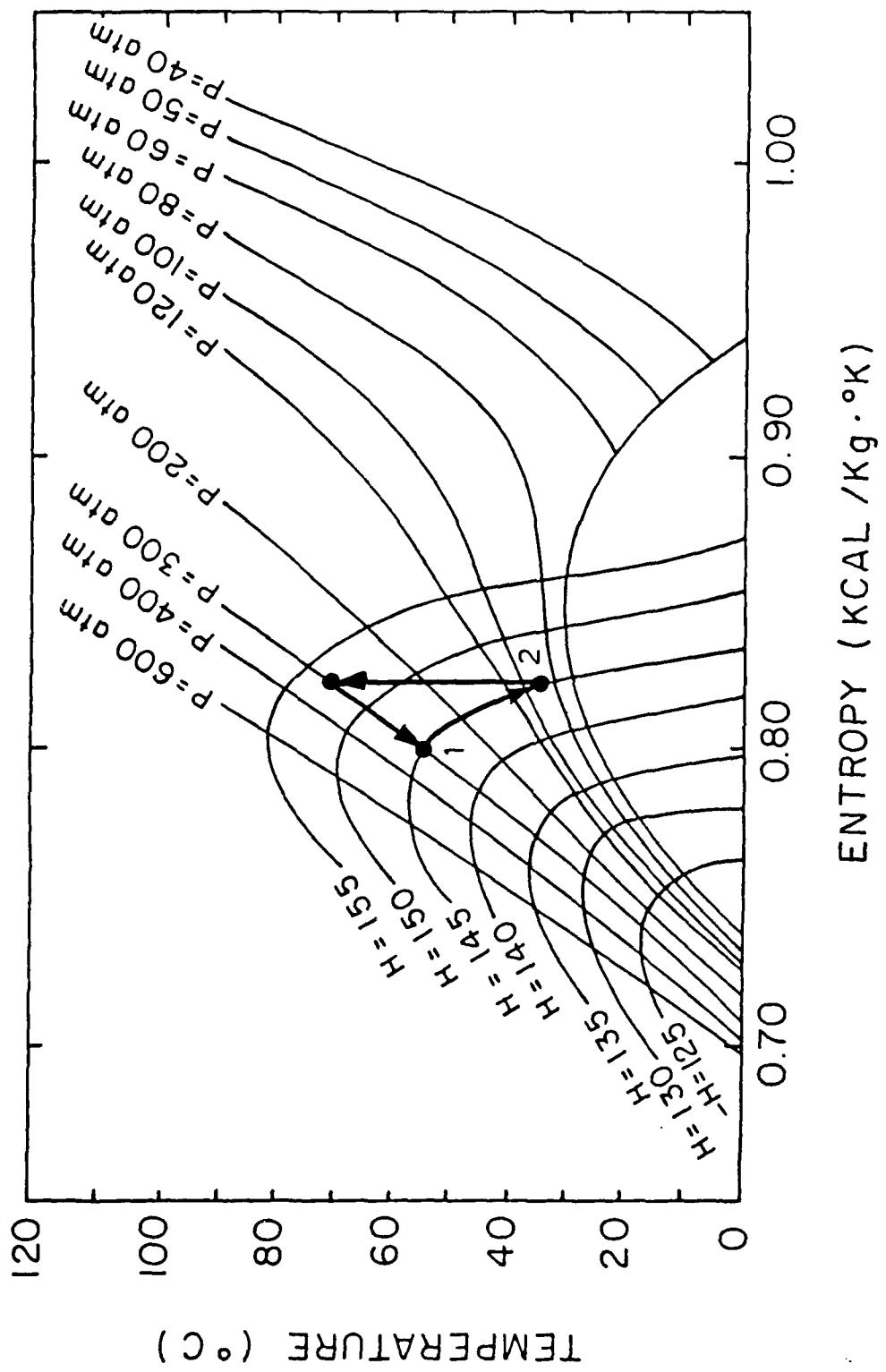
Figure 3. Tracing the Extraction Process on a Mollier (Temperature-Entropy) Diagram

with the formation of solid naphthalene are ignored for this discussion.) The stream of carbon dioxide leaving the separator is now at $36^{\circ}C$ and 90 atm. As this stream is isentropically compressed to 300 atm, its temperature rises to $72^{\circ}C$. The energy required to compress CO_2 to 300 atm, can be read directly from the Mollier diagram; the energy is 7 kcal/kg (12.6 Btu/lb) of CO_2. In completing the process cycle the CO_2 stream is isobarically cooled to $55^{\circ}C$, the initial extraction temperature, (and no attempt is made here to integrate the heat-exchange steps in this process to improve the energy efficiency). Since the expansion of CO_2 results in a solubility decrease from 15 wt-% to 2.5 wt-%, it is readily calculated that it is necessary to recycle about 6.7 pounds of CO_2 to extract one pound of naphthalene.

The energy required to extract naphthalene via the Path 1-2 is compared to the energy needed to vaporize naphthalene from the chalk dust mixture. The electrical energy required to compress 6.7 lbs of CO_2 in the recycle stream (at 12.6 Btu/lb CO_2) is 84.4 Btu, i.e., that is the electrical energy input to the process to extract one pound of naphthalene, and the equivalent thermal energy of this step is about 222 Btu assuming 38% Carnot efficiency, i.e., the conversion of heat of combustion energy from natural gas or coal to electrical energy, is 38%. The vaporization process for naphthalene separation requires energy input for latent and sensible heat. The heat of vaporization is 84 Btu/lb naphthalene, and in order to raise the bed temperature from ambient to $218^{\circ}C$ (the boiling point of naphthalene) a sensible heat input of 350 Btu/lb naphthalene is required. Thus, the total thermal energy requirement for the vaporization process is 434 Btu/lb naphthalene, while in this separation, while example extraction with supercritical carbon dioxide requires only about one half the energy of the vaporization process. It is seen that from Figure 2 the solubility of naphthalene in CO_2 is also influenced by temperature. Changing the temperature of a system can have a dramatic or moderate effect on the solubility behavior, depending on the region of the solubility diagram in which the change occurs. Thus, as an alternative to extraction and separation using pressure reduction, the process can operate isobarically using changes in temperature. For example, starting at point 1 of Figure 2, the stream leaving the extractor can flow through a heat exchanger (which is not shown in the figure) instead of a pressure-reduction valve and it can be cooled to $20^{\circ}C$, as indicated by the arrow on the 300-atm isobar. As the CO_2-rich stream is cooled, the concentration of naphthalene decreases from 15 wt-% to 3.6 wt-%, as shown by point 3. The carbon dioxide leaving the separator can then be heated back to $55^{\circ}C$ and recycled to the extractor. This isobaric mode of operation employs a blower, as compared with the compressor required in the previously described pressure-decrease mode of operation. The recycle ratio, as calculated from the solubility data shown in Figure 2, for this mode of operation is about 7.5 pounds of CO_2 per pound of naphthalene.

Temperature variations can be used advantageously in another region of the solubility diagram, the "low"-pressure region or retrograde-condensation region where increasing temperature causes a decrease in solubility. Specifically, for the case of the naphthalene-chalk dust separation, the process can operate isobarically between points 4 and 5 in Figure 2. Extraction occurs at 80 atm and $32^{\circ}C$ and recycled to the extractor. The solubility levels are lower, but so are the operating pressure levels, and the economics of this mode of operation must be compared with the previous modes for each specific case.

A fourth alternative for carrying out the naphthalene extraction utilizes the dissolving capacity of near-critical liquid carbon dioxide. This operating mode is illustrated in Figure 2 by the L-V tie line. Liquid carbon dioxide is employed to dissolve and extract the naphthalene

from the mixture, and the solution leaving the extractor is heated to vaporize the carbon dioxide and recover the naphthalene. The CO_2 is then condensed and recycled to the extractor.

In summary of extraction with gases, there exist four modes of operating the extraction of solid (or other) substances. The specific mode employed in any instance is a function of many factors, for example, the sensitivity of the material(s) to temperature and the ease of condensation or nucleation. Many facets and parameters must be considered and evaluated before a process and operating conditions are selected for any type of process; supercritical fluid extraction is no exception to this rule.

2.   Continuous Fractionation of Liquid Polymers with Supercritical Fluids

The simple extraction process described above can be extended to a multiple fraction separation process this is especially applicable to a many polymers and oils.

A schematic diagram of continuous fractionation system employing a supercritical fluid to separate the homologous-series members of a polymer is shown in Figure 4. Four extraction/separation vessels are (arbitrarily) shown in this figure. During operation of the fractionation process a liquid polymer is pumped in at the top of the primary contacts, and since the density of the gas will probably be less than that of the polymer, the gas is introduced at the bottom of the column. The extract phase leaving the vessels contains those components which have dissolved in the gas at their solubility level, is consistent with the solubility characteristics of the polymer and the operating parameters in the vessel. In the figure, a "heavy" fraction is shown leaving the primary contractor vessel. If the extraction conditions are changed, the entire feed could just as easily be dissolved. The solution of the dissolved components and the gas is expanded to some lower pressure in the first separator; the highest-molecular-weight oligomers in the solution precipitate. The remaining stream is stagewise reduced in pressure through the expansion valves to fractionate the polymer. After expansion to the lowest pressure, the (almost) solute-free gas is recompressed and recycled. The number of fractions that are obtained is consistent with the number of pressure-reduction stages, and the molecular-weight range of each fraction is related to the ratio of pressure reduction per stage.

Questions of the capital and operating costs of the batch extraction and fractionation processes cannot be generally given a priori. They will depend upon the operating conditions, materials of construction, degree of control, and many other factors and these same factors, of course, must be considered for any process. Even a "simple" distillation can vary in costs, both capital and operating, by one or two orders of magnitude because of these factors. However, because it is desired here to give a feel for the potential of supercritical fluid extraction in this propellant binder application, some costs for coffee decaffeination for a plant producing 50,000,000 lbs/yr are related. No absolute figures have been published, but the "rumors and hearsay" in the supercritical fluid "community" give a figure between $0.30-0.50/lb of coffee. Perhaps an absolutely outside figure is based on the retail price difference between Maxwell House (the supercritical fluid coffee decaffeinator) and Sanka brand coffee. For 13 oz of Maxwell House coffee the price is $2.89 while for Sanka it is $4.19, for a total delta of $1.30/13 oz or $1.60/lb. Maxwell House is probably not selling Sanka for only a decaffeination cost differential, so the $1.60 figure is assuredly high. As will be seen later when the economic evaluation is carried out (Section IV) the cost of processing 10,000,000 lbs/yr of propellant binder is less than $1/lb.

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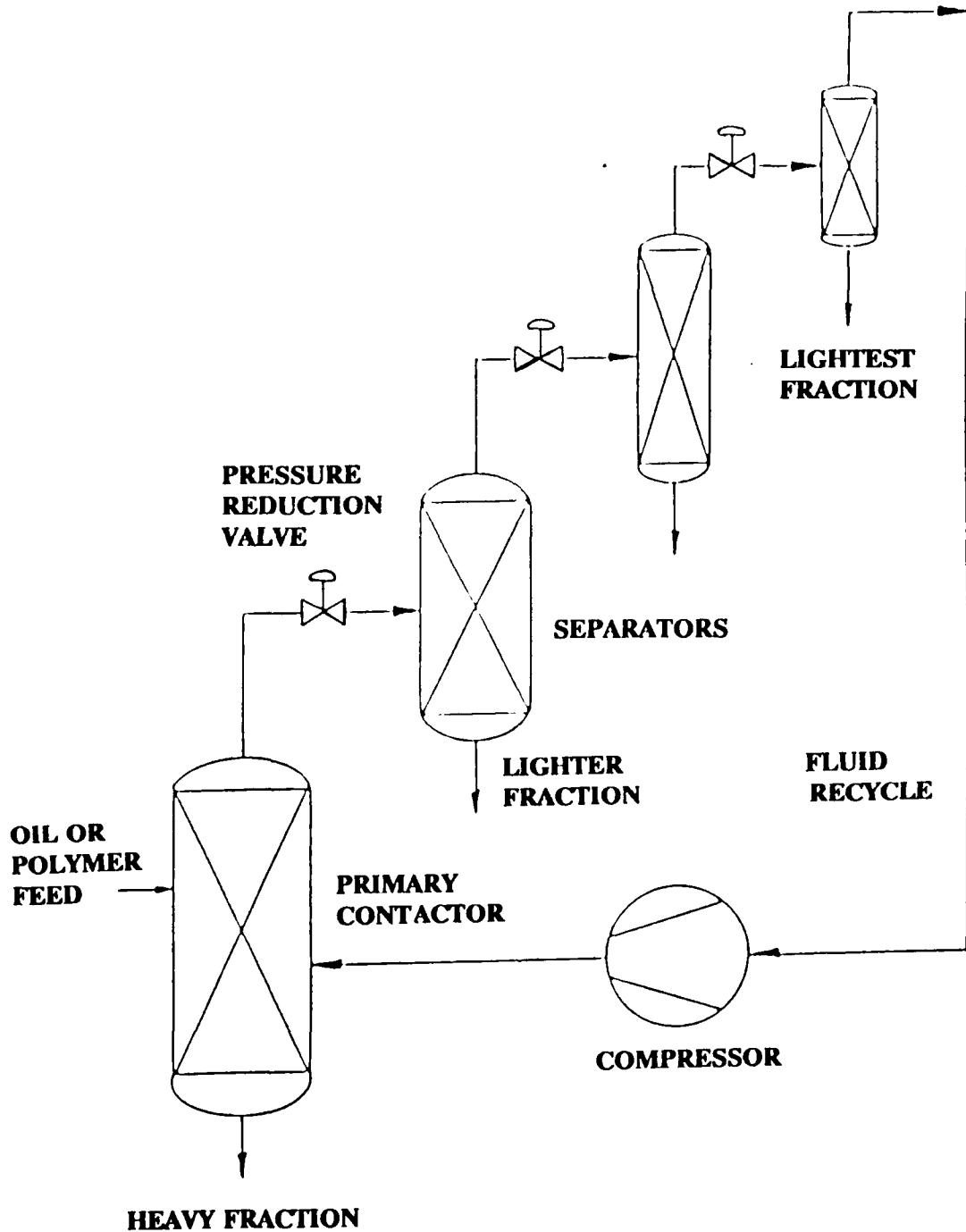
Figure 4. Schematic Diagram of a Supercritical Fluid Fractionation Process

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III. EXPERIMENTAL METHODS AND RESULTS

A. Selection of Candidate Materials

Two polymers, hydroxy-terminated polybutadiene (HTPB) and glycidyl azide polymer (GAP) were selected by the Astronautics Laboratory, Edwards AFB for evaluation in this program. The precursor to GAP, polyepichlorohydrin (PECH) was also tested. PECH is converted to GAP by reaction with sodium azide.

HTPB has been a standard propellent binder for years despite its notorious heterogeniety and lot to lot variation. The Air Force has commisioned a number of studies in an attempt characterize HTPB and relate physical properties of the polymer to performance properties of the binder. These studies including Laub (2), Ramey (3), Blanks et al. (4), Stephens et al. (5) have demonstrated heterogeneity inherent to HTPB.

GAP possesses several desireable performance properties, including its energetic and smokeless characteristics. Commercial development however, has been slowed by problems such as off-gasing. While a definitive cause of the performance problems has not yet been established there is much speculation that it may be related to the presence of low molecular weight and non-functional oligomers and other impurities present in the final product.

There are three primary motives for fractionating HTPB and GAP. As an analytical tool, analysis of the fractionated samples can elucidate the molecular weight dependancece of critical properties such as fuctionality and determine the feasibility of removing other interfering species. The second motivation is to generate large samples of the fractions for formulation and casting. Performance testing of these samples provide a means for directly evaluating the performance of the binder as a function of molecular weight and molecular weight dependent properties. Finally, once the optimal and deleterious fractions have been identified the polymers may be processed to provide a source of pre-propellant binder with consistent and optimized properties.

B. Apparatus, Techniques and Results

1. Experimental Equipment

A schematic of the apparatus used for the fractionation of HTPB, GAP, and PECH is given in Figure 5. A complete description of the equipment is provided elsewhere (8) and therefore is only briefly described here. The primary components of the system include the gas supply, a diaphragm compressor and pressure controller, a surge tank/preheater, a 60 ml extraction vessel, a heated valve and U-tube collectors for recovery of the polymer. Gas flow rate is measured by a rotameter and total gas flow by a dry test meter.

The polymers were fractionated by the conventional means of an isothermal pressure profile in a laboratory scale batch-continuous manner. In a typical fractionation the polymer is loaded in the extractor and solvent admitted to the vessel from the surge tank/preheater. The solvent preferentially dissolves the material of high solubility as it traverses the column. Upon exiting

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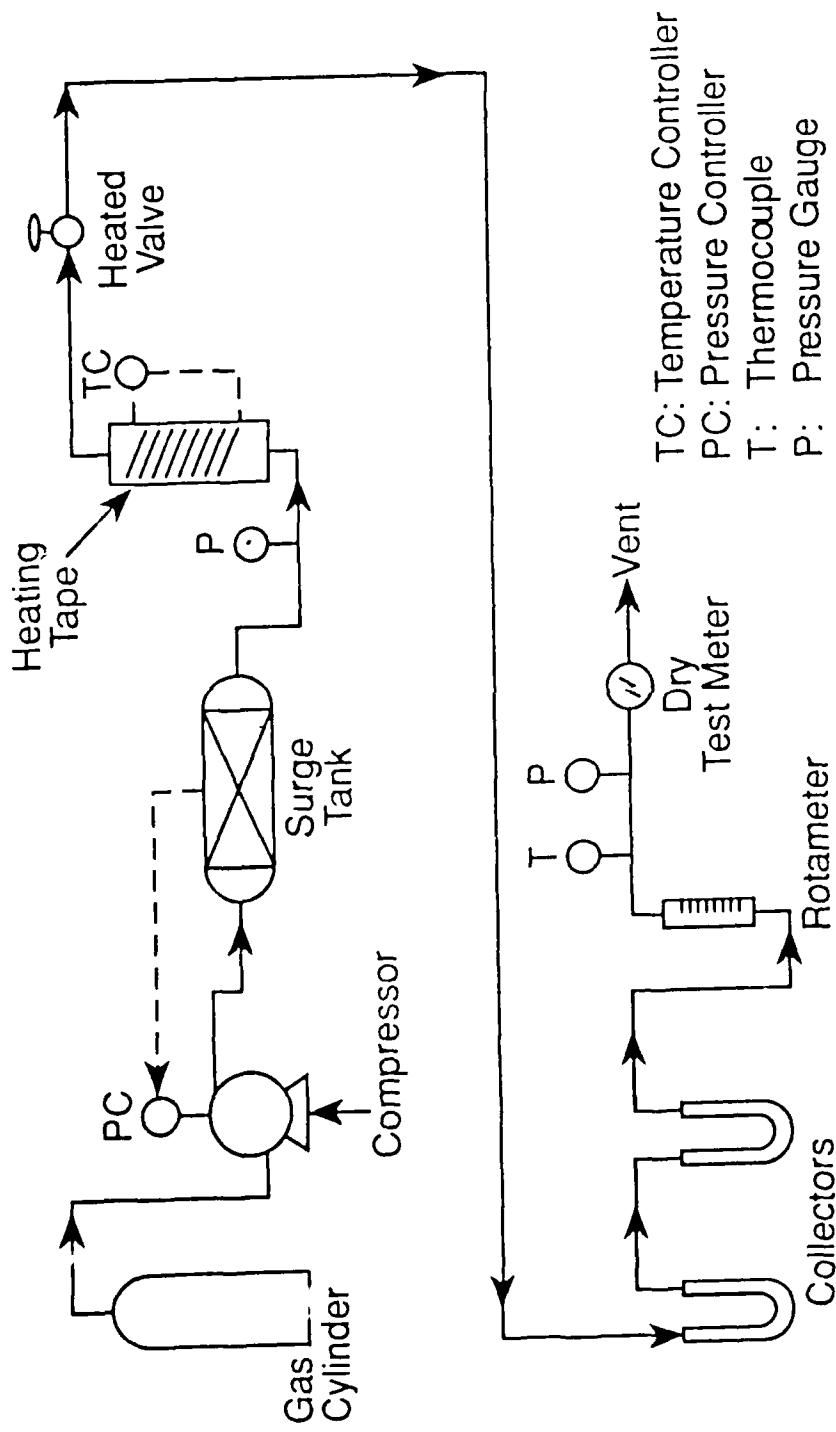
Figure 5. Schematic of a SCF Extraction System

TC: Temperature Controller
PC: Pressure Controller
T : Thermocouple
P : Pressure Gauge

the column the fluid is expanded via the pressure reduction valve resulting in the precipitation and collection of the solute in the U-tube collectors. The solvent rapidly dissipates and may be recycled to the gas supply or vented. In general a given pressure level is maintained until the fraction which is soluble at that condition is depleted as evidenced by the cessation of material precipitating from the expanded solvent. Pressure is then increased incrementally and the next fraction collected.

The R-45M samples were analyzed at the Astronautics Laboratory by GPC for molecular weight and molecular weight distribution and by FTIR for hydroxyl equivalent weight. The GAP samples were analyzed by reverse phase HPLC at The 3M Company. PECH samples were analyzed by gas chromatography using mass spectrometry detection. Selected fractions were also analyzed by mass spectrometry. Analysis for the PECH samples was also provided by The 3M Company.

2. Supercritical Fluid Processing of HTPB

a. Objective and Summary of Results

Several aspects of supercritical fluid processing of R-45M were investigated in this program. The first objective was to determine the feasibility of fractionating R-45M across the entire molecular weight distribution. It was found that HTPB is easily fractionated in propane. GPC and FTIR analysis indicated that the increase in hydroxyl equivalent weight was non-linear with respect to molecular weight resulting in a rapid increase in functionality in the high molecular weight fractions. This result is consistent with the Top-20 theory of Stephens, Campbell and Webb. The results of a small scale (ca 12g) and large scale (ca 140g) fractionation are discussed subsequently.

Low pressure liquid propane was evaluated as a potential solvent for removing the low molecular weight material from HTPB at very moderate temperatures and pressures. While liquid propane was expected to be substantially less selective than supercritical propane, the extractions were surprisingly effective in removing only the lower molecular weight material. Both small (ca 10g) and large (ca 228g) extractions demonstrated the viability of the low pressure process. The maximum pressure utilized in these extractions was 1200 psig. The tests are discussed in more detail subsequently.

The Astronautics Laboratory expressed an interest in evaluating the refractionation of a mid-cut of R-45M obtained from a previous fractionation. The refractionation produced expected results, i.e., fractions of a more narrow distribution were obtained from the mid-cut and fell within the expected distribution.

The effect of SCF extraction on the free water content of R-45M was the final line item investigated. Extractions with ethane and propane were found to have little effect on water content. The tests are discussed in further detail below.

b. Materials and Solvents

A commercially available sample of HTPB (R-45M) was obtained from Atochem North America for the experiments described in this report. The manufacturer lists the number

average molecular weight for R-45M as 2800 and gives a hydroxyl value of 0.70 meq/g for this batch. CO_2 and propane were evaluated as potential solvents for HTPB. Carbon dioxide was found to dissolve

approximately 12% of HTPB at temperatures up to 70°C and pressures up to 8500 psig. Propane was found to dissolve virtually all of the parent material at moderate pressure and therefore was the solvent of choice for almost all of the tests described subsequently.

c.   Fractionation with Propane

The first fractionation of HTPB was carried out in propane at 130°C. A 12g sample was separated into 10 fractions in the manner described in the apparatus and techniques section. The first nine fractions were obtained between 500 and 4900 psig. The final fraction was dissolved at high pressure (7500-8000 psig) and, therefore, high solubility levels to expedite the experiment. A summary of the fractionation conditions, fraction weights, and weight fraction (w_i) of each cut is given in Table 2. The summation of the weights of the col' 'ed fractions exceeds that of the charge because the fractions were weighed immediately after collecteion when residual, dissolved propane remained in the fractions. The dissolved propane completely desorbs after several hours.

TABLE 2

PBRM-2
Fractionation of HTPB with Supercritical Propane

$$T = 130°C, Charge = 12.12g$$

Fraction	Pressure Range (psig)	Standard Liters Solvent	Mass Collected (g)	w_i	Σw_i
1	500-800	450	0.48	0.034	0.034
2	1800-2400	640	1.30	0.092	0.126
3	2200-3000	540	1.67	0.119	0.245
4	2800-3000	730	1.37	0.097	0.342
5	3000-3400	810	1.15	0.082	0.424
6	3400-3800	630	1.08	0.077	0.501
7	3600-4000	620	1.20	0.085	0.586
8	4000-4600	640	1.24	0.088	0.674
9	4400-4900	1000	1.28	0.091	0.765
10	7500-8000	550	3.31	0.235	1.000

The fractions and a control sample were analyzed for molecular weight by GPC and hydroxyl equivalent weight by FTIR. The results are presented in Table 3 and shown graphically in Figure 6. The control was found to have a M_n of 2956, a M_w of 6253 (M_w/M_n = 2.12) and a hydroxyl equivalent weight of 1256 (0.796 meq/g). The fractions were found to have number

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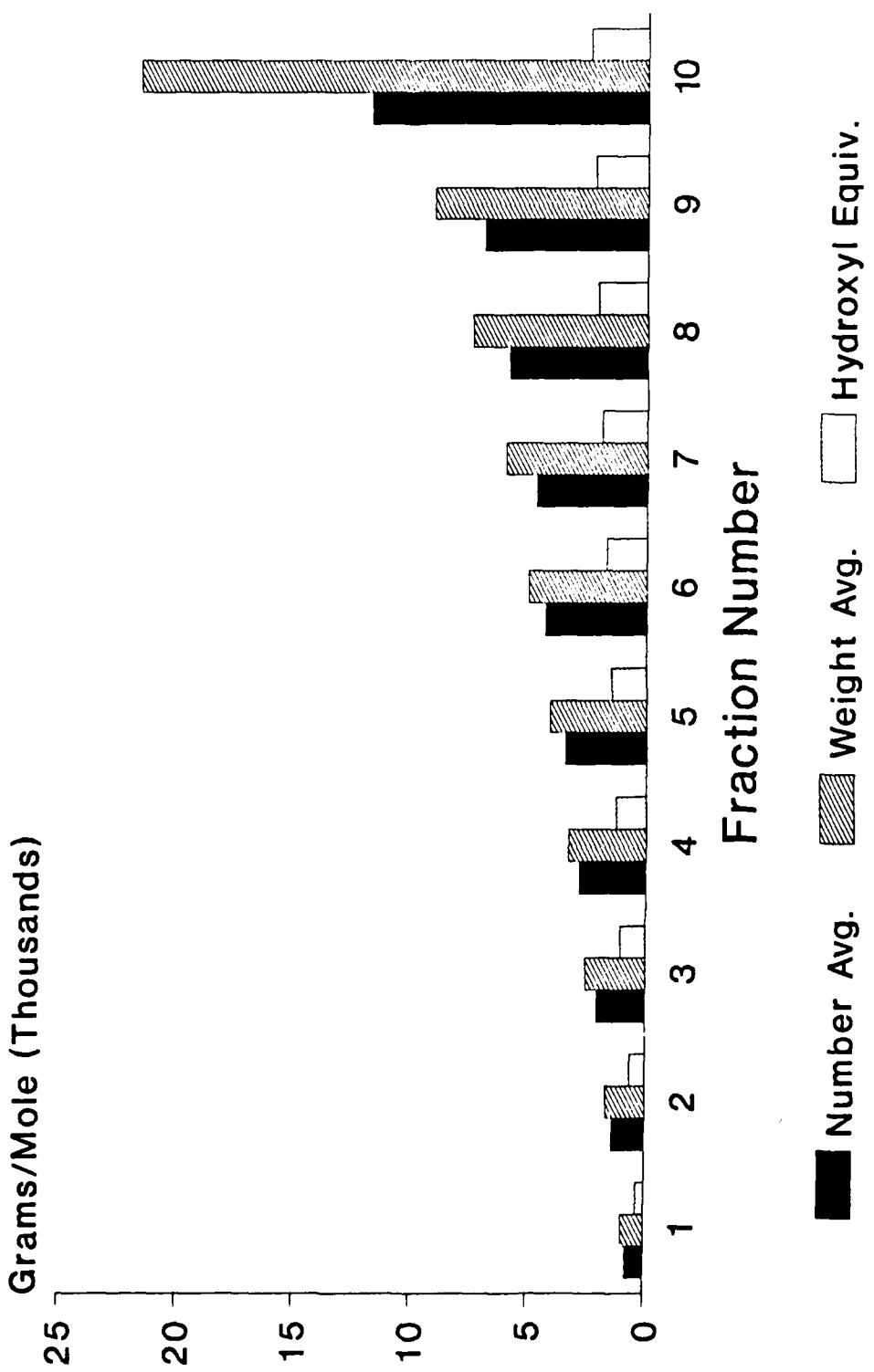
Figure 6. Analysis of PBRM-2 Fractions

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average molecular weights ranging from 781 to 11757 and weight average molecular weights from 969 to 21539 resulting in polydispersities of the order of 1.2. The increase in hydroxyl equivalent weight was found to be nonlinear with molecular weight especially in the latter fractions (see Figure 6) As a result, both number average functionality, F_n, and weight average functionality, F_w, increased markedly in the last two fractions. F_n ranged from 1.98 to 4.85 and F_w from 2.44 to 8.88. The dependence of functionality on molecular weight can be seen readily in Figure 7, a plot of F_n vs. M_n and Figure 8, a plot of F_w vs. M_w. The rapid increase in functionality is indicative of branching in the high molecular weight material and may have a profound effect on the cure properties of the final HTPB resin. Viscosities of the ten fractions from the propane fractionation were not measured, but as determined visually the fractions exhibited a clear trend in increasing viscosity with fraction number (and molecular weight).

TABLE 3

PBRM-2

Analysis of HTPB Fractions

Fract.	M_n	M_w	M_w/M_n	OH Eq. wt.	F_n	F_w
1	781	969	1.24	354	2.21	2.73
2	1409	1688	1.20	650	2.17	2.59
3	2063	2540	1.23	1041	1.98	2.44
4	2828	3299	1.17	1268	2.23	2.60
5	3450	4113	1.19	1481	2.33	2.78
6	4304	5013	1.16	1705	2.52	2.94
7	4691	6006	1.28	1902	2.47	3.16
8	5858	7423	1.27	2073	2.83	3.58
9	6936	9050	1.30	2200	3.15	4.11
10	11757	21539	1.83	2426	4.85	8.88
Contr.	2956	6253	2.12	1256	2.35	4.98

The functionality distribution is consistent with the data of Stephens, Campbell and Webb who fractionated micro samples of HTPB (ARCO Lot 5081) via GPC[5]. Their data are given in Table 4 and a graphical comparison of their work and the data of the present study is given in Figures 9 and 10 which show F_n and F_w of each fraction as a function of cumulative weight. The work at Thiokol Huntsville led to the development of the Top-20 theory which proposes that the mechanical properties of the propellant are determined almost exclusively by the properties of the highest molecular weight portion of the polymer (i.e., the top 20%). The theory could not be tested directly, in part because fractionation by GPC can not be scaled beyond micro-samples. SCF Fractionation offers the opportunity to generate large samples for performance testing and to positively identify and optimize the performance-property relationship of various fractions of HTPB.

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Figure 8. Functionality of HTPB Fractions - F_w vs. M_w

Figure 7. Functionality of HTPB Fractions - F_n vs. M_n

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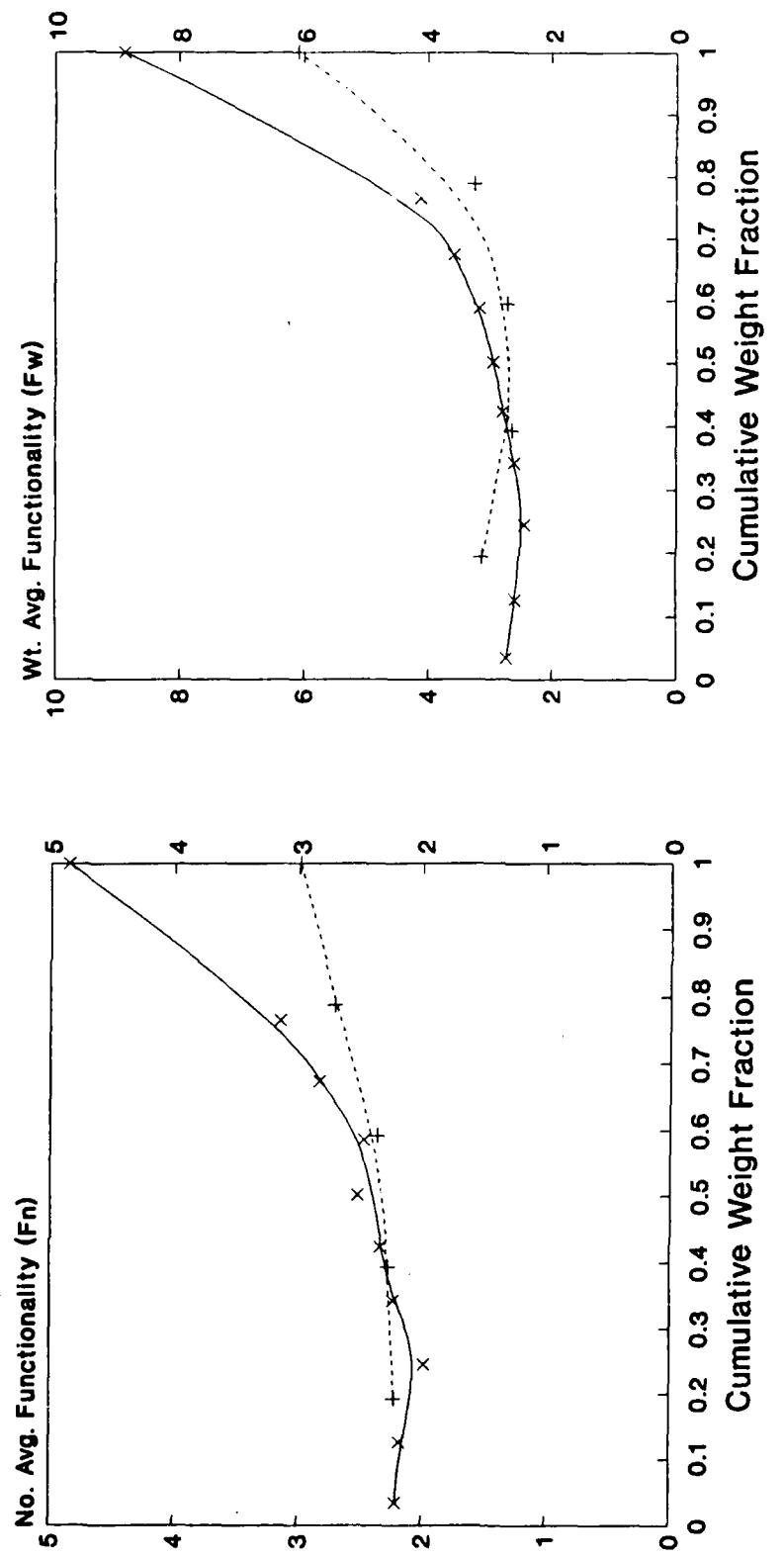
Figure 9. Cumulative Weight Fraction vs. F_n

Figure 10. Cumulative Weight Fraction vs. F_w

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TABLE 4

GPC Microfractionation of HTPB (ARCO Lot 5081)*

Fract.	w_i	M_n	M_w	M_w/M_n	F_n	F_w
5	0.193	1498	2102	1.40	2.22	3.12
4	0.200	2991	3489	1.17	2.27	2.64
3	0.200	4408	5059	1.15	2.36	2.71
2	0.195	6738	8057	1.20	2.71	3.24
1	0.211	9701	19764	2.04	2.99	6.09
Contr.	----	3313	7917	2.38	2.39	5.72

* Data from Stephens, Campbell, Webb (1977)

The fractionation of HTPB was scaled up to approximately 140g. A summary of the fractionation is presented in Table 5 and the analysis is presented in Table 6 and shown graphically in Figure 11.

TABLE 5

PBRM-3
Scale-up of HTPB Fractionation

T = 130°C, Charge = 140g

Fraction	Pressure Range (psig)	Standard Liters Solvent	Mass Collected (g)	w_i	Σw_i
1	1000-2200	2160	12.27	0.109	0.109
2	2400-2600	550	12.28	0.109	0.219
3	2900-3200	1770	11.45	0.102	0.321
4	3500-3700	1270	13.19	0.117	0.438
5	3700-4000	1400	12.24	0.109	0.547
6	4000-4200	1940	12.90	0.115	0.662
7	4200-4600	1950	11.80	0.105	0.767
8	4800-5200	3060	11.96	0.107	0.873
9	5400-7800	4000	8.23	0.073	0.947
10	Residual	----	~6.0	0.053	1.000

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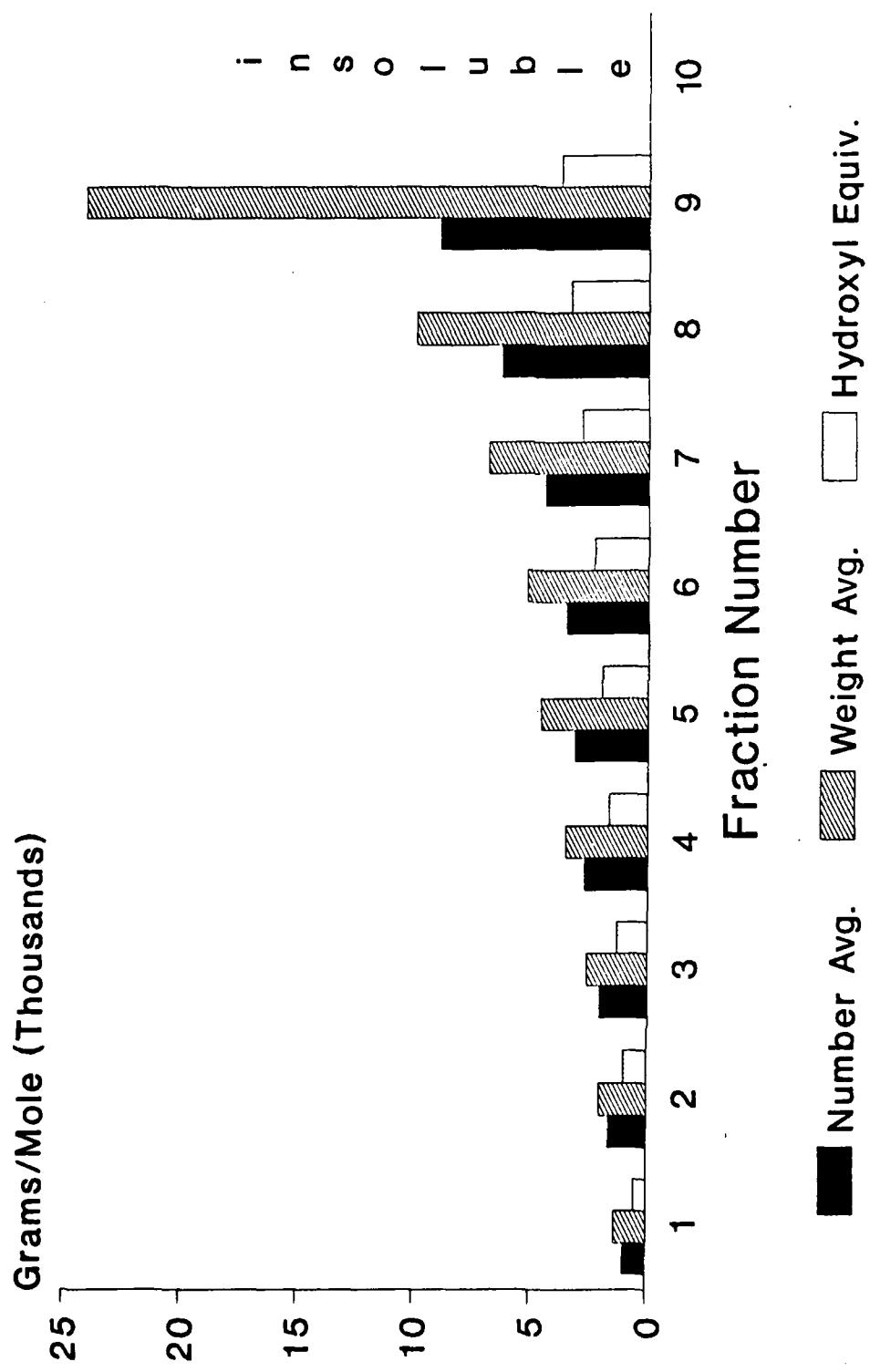
Figure 11. Analysis of PBRM-3 Fractions

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TABLE 6

PBRM-3
Analysis of Fractions from Large Fractionation

Fract.	M_n	M_w	M_w/M_n	OH Eq. Wt.	F_n	F_w
1	978	1370	1.40	537	1.82	2.55
2	1625	2023	1.24	974	1.67	2.08
3	2058	2580	1.25	1302	1.58	1.98
4	2695	3508	1.30	1634	1.65	2.15
5	3132	4546	1.45	1952	1.60	2.33
6	3497	5145	1.47	2298	1.52	2.24
7	4396	6821	1.55	2824	1.56	2.42
8	6244	9892	1.58	3288	1.90	3.01
9	8891	24009	2.70	3726	2.39	6.44
10*	----	-----	----	----	----	----
Control	2622	5479	2.09	1513	1.73	3.62

While absolute values of OH Eq Wt may be somewhat suspect in light of a comparison of the data obtained for the PBRM-2 control vs the PBRM-3 control, the trends in terms of molecular weights and functionality are very similar to that of PBRM-2. Interestingly, a solid insoluble residue has been identified in this fractionation. Two possibilities exist for the origin of the insoluble material. First, such residues are not uncommon in HTPB resins, especially those which are aged. The second possibility is polymerization in the fractionation equipment. When such a large and meticulous fractionation is attempted in a batch continuous manner on a laboratory system, the bulk of the material is exposed to process temperature for an inordinate amount of time. In this case some of the material was held at 130°C for 16 hours. It is possible that at these temperatures (despite the propane blanket) some crosslinking occurred. Fortunately, the residence time for the resin in a countercurrent process such as would be used for pilot plant testing or production would be much shorter, likely of the order of minutes. Further work is required in order to draw meaningful conclusions with regard to the residue.

d. Low Pressure Stripping of R-45M

Low pressure liquid propane was evaluated as a means of removing the low molecular weight fraction of HTPB. Liquid propane has the obvious advantages of moderate temperature and pressures. A small preliminary extraction was run at 40°C and is summarized in Table 7. It

was found that approximately 13% of the material could be removed at pressures below 800 psig. A larger scale extraction (ca 228g) was run at 60°C and pressures up to 1200 psig. The test is summarized in Table 8. The fractions were analyzed by GPC and FTIR and the results presented in Tables 9.

TABLE 7

PBRM-8
Small Scale Extraction of HTPB with Liquid Propane

$T = 40°C, Charge = 10.42g$

Fraction	Pressure Range (psig)	Standard Liters Solvent	Mass Collected (g)	w_i	Σw_i	$y_i\%$
1	500 - 800	190	0.72	0.069	0.069	0.21
2	500 - 800	160	0.66	0.063	0.132	0.23
Raffinate	----	----	~9.04	0.868	----	---

TABLE 8

PBRM-10
Scale-up of Extraction of HTPB with Liquid Propane

$T = 60°C, Charge = 228g$

Fraction	Pressure Range (psig)	Standard Liters Solvent	Mass Collected (g)	w_i	Σw_i	$y_i\%$
1	500 - 800	320	2.30	0.010	0.010	0.40
2	700 - 900	1310	8.80	0.039	0.049	0.37
3	800 - 1000	1100	7.10	0.031	0.080	0.36
4	900 - 1100	1700	7.90	0.035	0.115	0.26
5	1000 - 1200	1600	6.40	0.028	0.143	0.22
Raffinate	----	----	195.	0.875	----	----

TABLE 9

PBRM-10
Analysis of Liquid Propane Extracts of HTPB

Fract.	M_n	M_w	M_w/M_n	OH Equiv. Wt.	F_n	F_w
1	750	1200	1.60	420	1.79	2.86
2	900	1400	1.56	440	2.05	3.18
3	1200	1700	1.42	530	2.26	3.21
4	1300	1800	1.38	610	2.13	2.95
5	1600	2100	1.31	680	2.35	3.09
Raff.	4200	7500	1.79	1390	3.02	5.40

The effect of pressure on solubility is much less pronounced in the liquid state as compared to the supercritical state at temperatures moderately above the critical point because of a much smaller pressure dependence on density.

The ability to fractionate HTPB with propane in the liquid state is a consequence of the fact that while propane will dissolve all of the parent material it remains a "relatively poor" solvent for HTPB. The fractionation is driven by preferential solubility of the lighter components in the solvent phase (i.e., the low molecular weight components have a higher distribution coefficient). While solubility measurements taken in a dynamic system are not true equilibrium solubility values, it may be seen that the solubility of HTPB in liquid propane is low, i.e., on the order of 0.3 wt% and drops with increasing fraction number (and molecular weight) despite modest increases in pressure. It is interesting to note that the solubility of HTPB in liquid propane at $60^\circ C$ is less than that in supercritical propane at $130^\circ C$, suggesting a positive temperature dependence on solubility despite the decreasing density of the solvent with increasing temperature.

Fractionation of HTPB with liquid propane across the entire molecular weight distribution appears promising and should be investigated.

e. Refractionation of a Mid-cut

The Astronautics Laboratory was interested in the refractionation of a mid-cut of R-45M obtained from a previous supercritical propane fractionation. In the experiment designated PBRM-6, a mid-cut of HTPB was obtained at $120^\circ C$ for refractionation in a separate experiment. The test is summarized in Table 10. Fraction 2 was recovered after approximately 50% of the parent material was extracted. The fraction has a mass of 3.05g and represented approximately 12.2% of the charge. Approximately 1.77 grams of Fraction 2 was refractionated into seven fractions in a separate experiment designated PBRM-7. The test is summarized in Table 11.

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TABLE 10

Test to Obtain a Mid-cut of R-45M To Be Subsequently Refractionated in Propane
PBRM-6

$$T = 120^{\circ}C, \text{Charge} = 24.90g$$

Fraction	Pressure Range (psig)	Standard Liters Solvent	Mass Collected (g)	w_i
1	1800-3400	1770	12.75	0.512
2	3400-3800	1030	3.05	0.122
3	Raffinate	----	9.10	0.365

TABLE 11

Refractionate Fraction 2 (PBRM-6) in Propane
PBRM-7

$$T = 120^{\circ}C, \text{Charge} = 1.77g$$

Fraction	Pressure Range (psig)	Standard Liters Solvent	Mass Collected (g)	w_i	Σw_i
1	≤2600	220	0.11	0.059	0.059
2	2600-2900	130	0.20	0.108	0.167
3	2900-3200	270	0.37	0.199	0.366
4	3200-3600	280	0.43	0.231	0.597
5	3600-3900	230	0.32	0.172	0.769
6	3900-4200	410	0.24	0.129	0.898
7	4200-4600	470	0.19	0.102	1.000

The extraction profile is typical of a refractionated sample. It is not surprising that the pressure limits of the refractionation do not precisely coincide with the original fractionation as the solubility of the fraction is no longer affected by lower molecular weight chains, which may act as entrainer, or higher molecular weight, which compete with propane as a solvent. The GPC analysis of the refractionated samples are presented in Table 12. As expected the refractionation resulted in cuts of low polydispersity and gradually increasing molecular weight.

TABLE 12

Analysis of Samples from PBRM-7
Refractionation of a Mid-cut of R-45M

Fraction	M_n	M_w	M_w/M_n
7-1	NA	NA	----
7-2	4170	6210	1.49
7-3	4420	6090	1.38
7-4	4850	6450	1.34
7-5	5650	7380	1.28
7-6	5770	7390	1.28
7-7	5550	7570	1.36

f.   Influence of SCF Extraction on Free Water Content

The Astronautics Laboratory was interested in whether supercritical fluid extraction would affect the free water content of R-45M. R-45M was extracted with ethane and propane in separate experiments and sent to Atochem North America for Karl Fisher analysis.

The two experiments PBRM-4, in which approximately 13 wt% of the charge was extracted with propane, and PBRM-5 in which approximately 15 wt% of the charge was extracted with ethane, are summarized in Tables 13 and 14.

TABLE 13

PBRM-4
Extraction of R-45M with Propane for H_2O Analysis

T = 120°C, Charge = 29.92g

Fraction	Pressure Range (psig)	Standard Liters Solvent	Mass Collected (g)	w_i
1	1200 - 2400	850	3.80	0.127
Raffinate	----	----	26.12	0.873

TABLE 14

PBRM-5
Extraction of R-45M with Ethane for H_2O Analysis

Charge = 29.42g

Fraction	Temp. °C	Pressure Range (psig)	Mass Collected (g)	w_i
1	60	4500-9500	3.34	0.114
2	80	9000-9500	1.05	0.036
Raffinate	----	----	----	0.850

The raffinate samples and a control were analyzed. The results presented in Table 15 indicate very little difference between a control sample (0.06% water) and the extracted sample (0.05% water respectively). In all cases the measured values fall well below the product specification of 0.10% maximum water content.

TABLE 15

Results of Karl Fisher Analysis

Sample	Water Content (%)
Control	0.06
PBRM-4 Raffinate (propane)	0.05
PBRM-5 Raffinate (ethane)	0.05

3. Supercritical Fluid Processing of GAP

a. Objectives and Summary of Results

While GAP is a very promising energenic binder for low smoke and no smoke propellant, several performance problems have haunted its commercial development. Among the most notorious of these is the propensity of some batches to demonstrate excessive nitrogen off-gassing. The material also contains a fraction of nonfunctional oligomers which may interfere with performance. While the causes of these performance problems have not been clearly identified, the low molecular weight fraction has been suspected as a culprit for some time.

The primary objective of processing GAP with supercritical solvents was to determine the feasibility of extracting the low molecular weight components of GAP. A secondary objective was to fractionate GAP across the entire molecular weight distribution. Complete fractionation implies complete dissolution of the polymer. Fractionation, therefore, is also inherently a purification procedure because any ionic impurities present in the polymer would be insoluble and therefore remain in the extractor. One subject of interest is the molecular weight dependence of functionality, i.e., is GAP analogous to R-45M in that due to branching the high molecular weight material exhibits a functionality significantly greater than the bulk?

The low molecular weight components of GAP were effectively extracted with carbon dioxide as evidenced by HPLC analysis. Extraction with propane was found to be slightly less effective than carbon dioxide. GAP was fractionated across the entire distribution with HCFC-22. The individual fraction demonstrated a color progression from light yellow to burnt orange. One school of thought supports the idea that the high molecular weight fraction is responsible for the dark color of GAP. Quantitative analysis for the HCFC-22 fractionation is not yet available. The tests and available analyses are presented in detail below.

b. Materials and Solvents

Two samples of GAP, L-11391 and L-9961, were obtained from 3M Company for the experiments described in this section. According to the manufacturer, L-11391 and L-9961 contain approximately 2.0% and 0.5% of nonfunctional cyclic oligomers respectively. L-9961 is made from a different synthetic process than L-11391 which is thought to eliminate most or all

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of the organic tin residual. GAP manufactured via the synthetic route of that used to produce L-9961 is the method of choice under consideration for producing commercial quantities of GAP.

Carbon dioxide, propane and HCFC-22 were evaluated as potential solvents for GAP. Both carbon dioxide and propane dissolved only the low molecular weight portion of the parent material at convenient operating temperatures and pressures. Carbon dioxide, in general, was found to be a better solvent than propane for GAP.

Liquid and supercritical HCFC-22 were found to dissolve virtually all of the parent material at moderate conditions and is suitable for fractionation of GAP across the entire molecular weight distribution.

c. Extraction with Carbon Dioxide

Both samples of GAP, L-11391 and L-9961 were extracted with carbon dioxide at 60°c and maximum pressures of 9400 and 9600 psig respectively. It was found that approximately 11.4 wt% of the L-11391 and 4.0 wt% of the L-9961 could be removed. It is not surprising that more of the L-11391 material was soluble or it is known to contain a larger fraction of low molecular weight materials. The tests are summarized in Tables 16 and 17.

TABLE 16

3MGP-2
Extraction of 3M GAP L-11391 with Supercritical CO_2

$$T = 60^\circ C, Charge = 15.33g$$

Fraction	Max Pressure (psig)	Standard Liters Solvent	Mass Collected (g)	w_i	Σw_i
1	2500	640	0.19	0.012	0.012
2	4200	620	0.75	0.049	0.061
3	7200	540	0.38	0.025	0.086
4	9400	600	0.43	0.028	0.114

TABLE 17

3MGP-3
Extraction of 3M GAP L-9961 with Supercritical CO_2

$$T = 60^{\circ}C, \text{Charge} = 15.26g$$

Fraction	Max. Pressure (psig)	Standard Liters Solvent	Mass Collected (g)	w_i	Σw_i
1	4600	1610	0.07	0.005	0.005
2	7200	1550	0.18	0.012	0.016
3	8600	770	0.17	0.011	0.028
4	9600	350	0.19	0.012	0.040

The fractions were analyzed by reverse phase HPLC and indicated the isolation and removal of the nonfunctional cyclics and oligomer fractions from the raffinate. Figures 12a and 12b show the chromatograms of a control sample of L-11391 and the raffinate from the extraction summarized in Table 6. It should be noted that the oligomer fraction is completely absent in the raffinate chromatogram. Figures 12c-f show the chromatograms of each of the isolated fractions. The peak eluting at 24.5 is thought to be an impurity from the test since it is not present in the parent fraction.

The HPLC chromatograms for the control L-9961 and each of the fractions from 3MGP-3 are shown in Figure 13. It can be seen that as compared to the L-11391 material there are fewer low molecular weight component. The chromatograms of the fractions indicate the ability to remove the low molecular weight material which is present in L-9961.
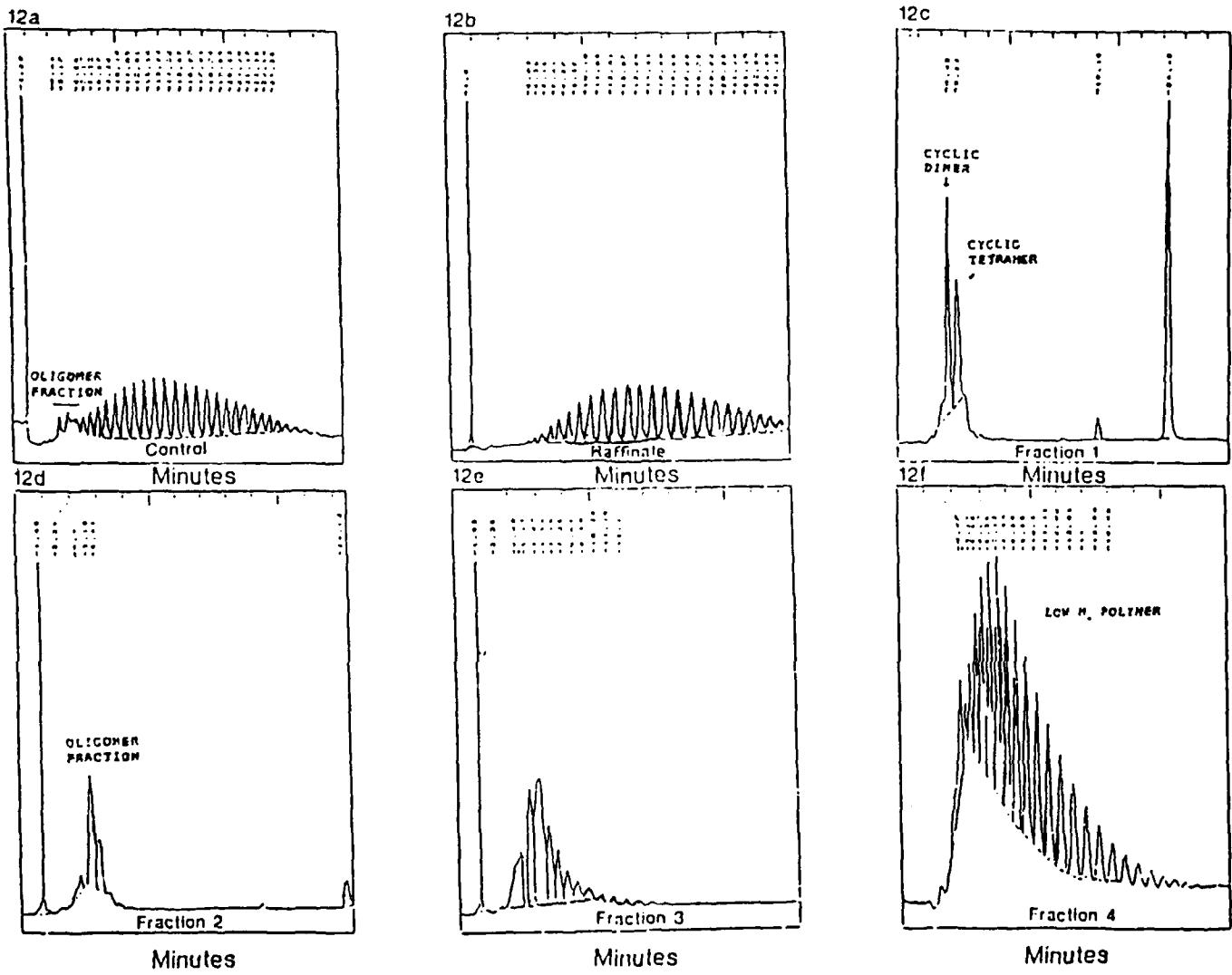
Figure 12.   Analysis of Fractions from Supercritical CO_2 Extraction of GAP L-11391
(Reverse Phase HPLC Chromatograms)

**3MGP-3 Fractions 1-4**
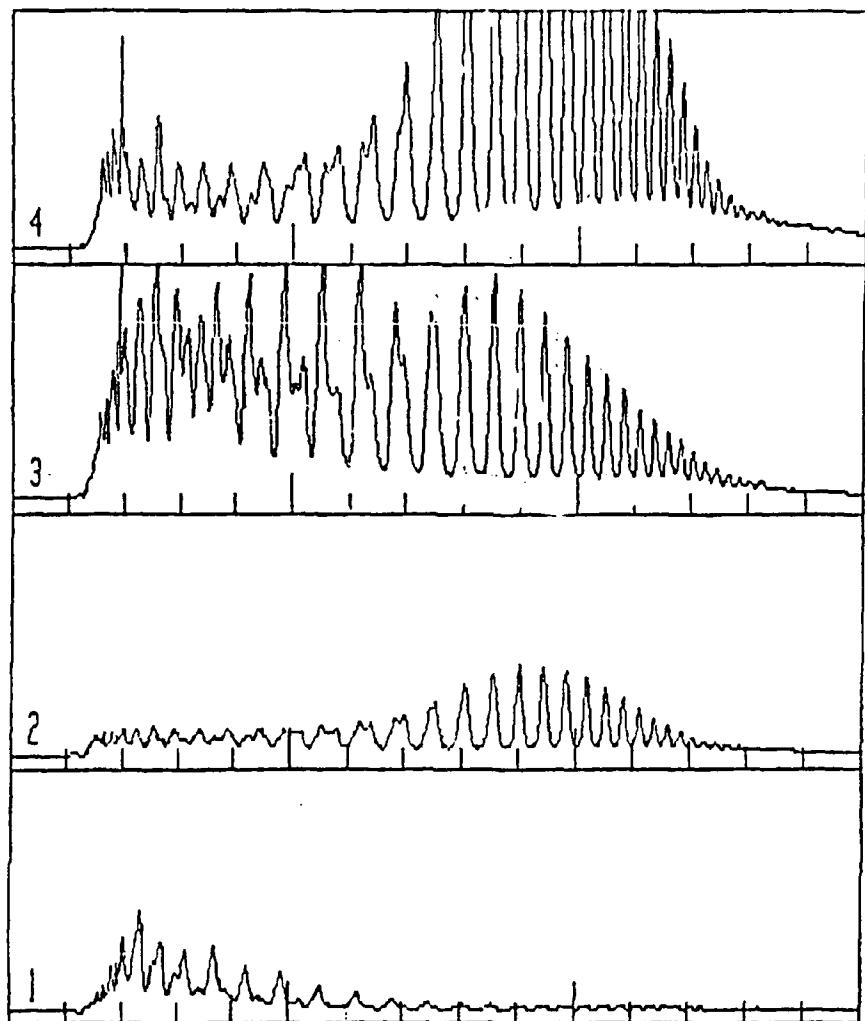
3MGP-3 Raffinate and Control
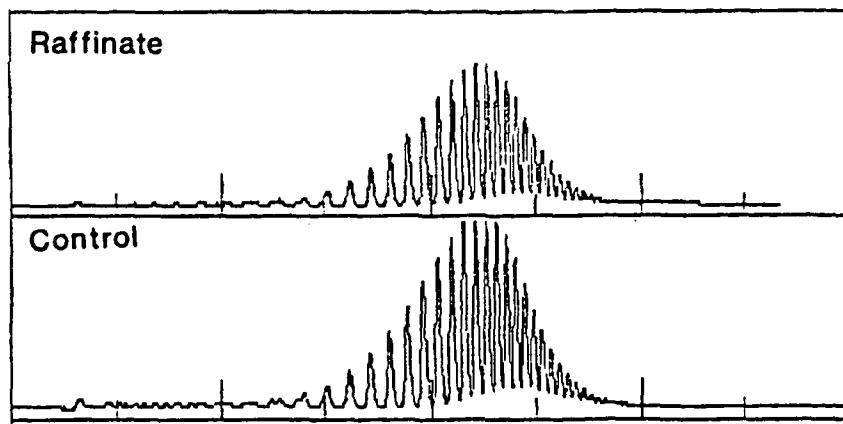
Figure 13.   Supercritical Carbon Dioxide Extraction of GAP l-9961
(Reverse Phase HPLC Chromatograms)

d. Extraction with Liquid Propane

Both samples of GAP, L-11391 and L-9961 were extracted with liquid propane at $60^{\circ}C$ and maximum pressures of 9800 and 9600 psig respectively. The extraction of L-11391 was designated 3MGP-5 and the extraction of L-9961 was designated 3MGP-4. Total extractables were found to be 6.5% and 1.4% of the parent material for L-11391 and L-9961 respectively at conditions summarized in Tables 18 and 19.

TABLE 18

Extraction of 3M GAP L-11391 with Liquid Propane
3MGP-5

$$T = 60^{\circ}C, \text{Charge} = 14.40g$$

Fraction	Max. Pressure (psig)	Standard Liters Solvent	Mass Collected (g)	w_i	Σw_i
1	2200	740	0.53	0.037	0.037
2	6500	960	0.23	0.016	0.053
3	9800	150	0.18	0.013	0.065

TABLE 19

Extraction of 3M GAP L-9961 with Liquid Propane
3MGP-4

$$T = 60^{\circ}C, \text{Charge} = 13.25g$$

Fraction	Max. Pressure (psig)	Standard Liters Solvent	Mass Collected (g)	w_i	Σw_i
1	2200	520	0.06	0.005	0.005
2	2500	1200	0.04	0.003	0.008
3	9600	1300	0.08	0.006	0.014

The HPLC chromatograms of each of the fractions and the raffinate samples are shown in Figures 14 and 15. It may be concluded that while propane does remove some of the low molecular weight material it is not as effective as CO_2.

3MGP-5 Fractions 1-3
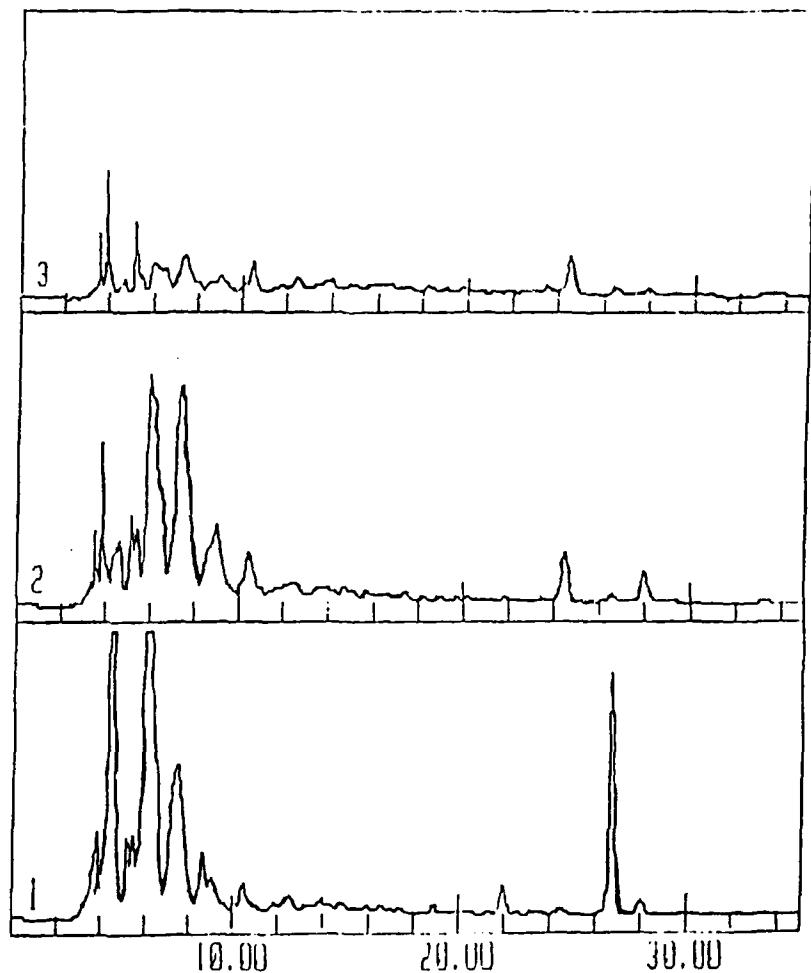
3MGP-5 Raffinate and Control
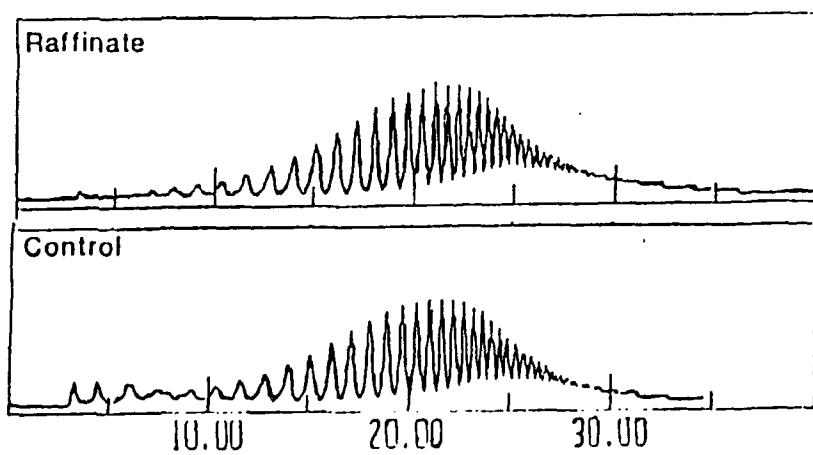
**Figure 14.**   Liquid Propane Extraction of GAP L-11391
(Reverse Phase HPLC Chromatograms)

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3MGP-4 Fractions 1-3
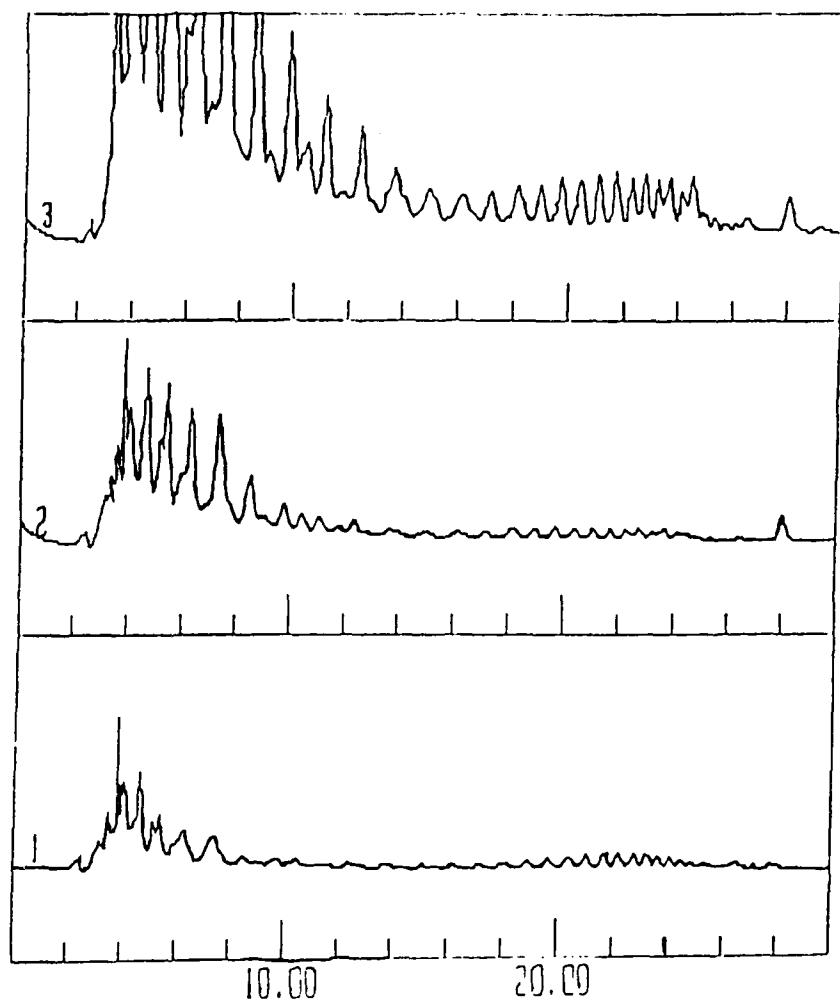

3MGP-4 Raffinate and Control
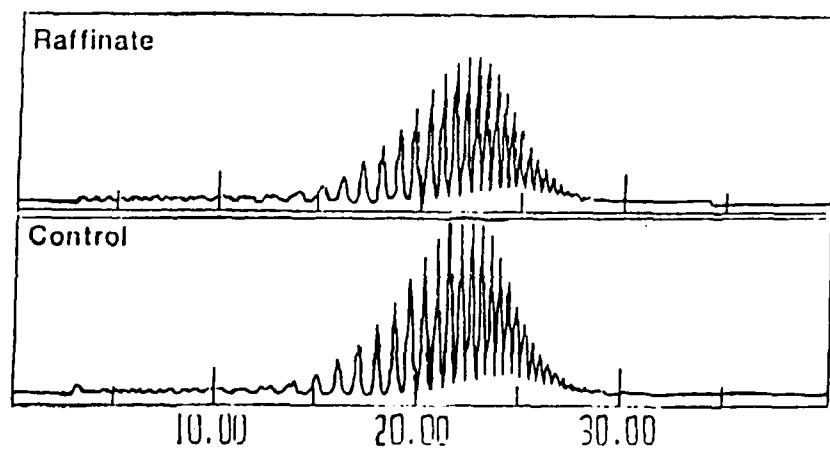
Figure 15. Liquid Propane Extraction of GAP L-9961
(Reverse Phase HPLC Chromatograms)

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e. Fractionation with Liquid HCFC-22

The original objective of the final test was to isolate a large sample of the oligomer fraction. This sample will be used in nitrogen evolution tests by Tony Manzara at 3M Company. One important goal of the test is to determine the role of the oligomer fraction in the off-gassing problem associated with some samples of GAP.

Approximately 102g of L-11391 was charged to a column and extracted with carbon dioxide at 45°C and pressures up to 9500 psig. Approximately 11.2% of the material was recovered in two fractions. Rather than terminating the experiment, it was continued in order to evaluate HCFC-22 as a potential solvent for GAP. It was found that HCFC-22 could dissolve virtually all of the parent material at modest temperature and pressures. The experiment is summarized in Table 20. Fractions 3-7 were collected at pressures up to 5200 psig. The large increment in pressure for the last fraction was used to expedite the experiment.

TABLE 20

3MGP-6
Fractionation of GAP (L-11391) with Carbon Dioxide and Liquid HCFC-22

$T = 45^\circ C$, Charge $= 101.7$g

Fraction	Solvent	Max. Pressure (psig)	Standard Liters Solvent	Mass Collected (g)	Σw_i
1	CO_2	5000	2160	4.66	0.044
2	CO_2	9500	2900	7.16	0.112
3	F-22	2600	430	15.97	0.263
4	F-22	3200	460	21.39	0.466
5	F-22	3200	600	20.63	0.661
6	F-22	3700	720	16.21	0.815
7	F-22	5200	1350	17.50	0.980
8	F-22	7000	650	2.07	1.000

While there was no analytical data available at the time this report was written, several important observations may be made of the fractions. The first two fractions (extracted with CO_2) are almost clear but have a slight pinkish color. The fractions extracted with HCFC-22 show a progression of color from a light greenish-yellow for fraction 3 to a very deep orange-brown in t e final two fractions. One theory suggests that the dark color associated with GAP is attributable to high molecular weight material. There is also a steady increase in viscosity across the fraction. This is especially obvious in the last fraction where the sample is virtually a gum. The probability for a successful fractionation by molecular weight using liquid HCFC-22 is high because despite its ability to dissolve the entire distribution, HCFC-22 is a relatively poor solvent for GAP. The solubilities observed during the extraction were on the order of 1 wt%. (The density of HCFC-22 is approximately 3.54g/standard liter).

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4. Supercritical Fluid Processing of Polyepichlorohydrin

a. Objectives and Summary of Results

The primary objective of processing PECH with supercritical fluids is to determine the feasibility of extracting the low molecular weight components from the parent material. PECH is the primary precursor to GAP, i.e., it is converted to GAP by reaction with sodium azide. It is hypothesized that the elimination of the low molecular weight material in PECH will result in GAP with substantially reduced oligomer content.

The low molecular weight material, including non-functional cyclics, was effectively extracted with supercritical propane as evidenced by G.C. analysis. It was also found that while CO_2 was not as effective as propane it could be used to extract some low molecular weight material.

b. Materials and Solvents

A commercially available sample of Polyepichlorohydrin (PECH), Dynamar HX-102 was obtained from the 3M Company for the experiments described in this section. It was found that approximately 7.3 wt% of the parent material could be extracted with carbon dioxide at $60^{\circ}C$ and pressures up to 9000 psig. It was found that approximately 12.2 wt% could be extracted with propane at $120^{\circ}C$ and pressures up to 9000 psig.

c. Extraction with Supercritical CO_2

A 20.0g sample of PECH was extracted with carbon dioxide at $60^{\circ}C$. The test is summarized in Table 21.

TABLE 21

3MPCH-1
Extraction of 3M PECH (Dynamar HX-102) with Supercritical CO_2

$T = 60^{\circ}C$, Charge $= 20.00g$

Fraction	Max. Pressure (psig)	Standard Liters Solvent	Mass Collected (g)	w_i	Σw_i
1	3800	440	0.38	0.019	0.019
2	9000	1080	1.08	0.054	0.073

The collected fractions were analyzed by gas chromatography using mass spectrometry detection. Only the low molecular weight material elutes from the column. The chromatograms from a control sample of Hx-102 and the two fractions from the CO_2 extraction are shown in Figures 16a-16c. It is believed that the peak at approximately 11 minutes represents a cyclic dimer.(18) The mass spectra of the elution peak at 24 minutes shows a major fragment at 371

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16a   Hx-102 Control
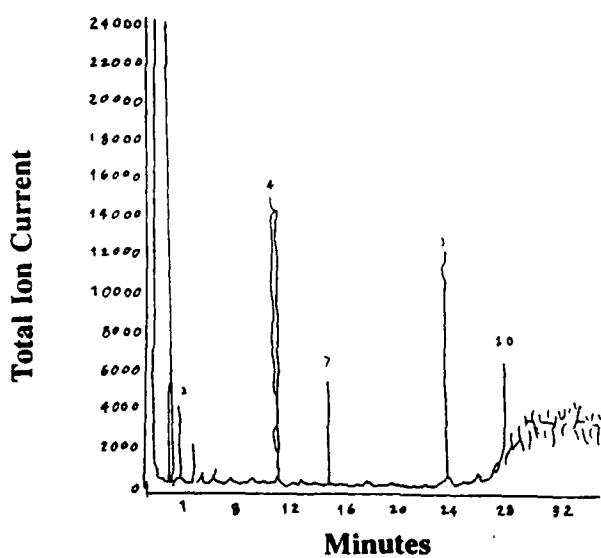
16b CO_2 Extraction Fraction 1
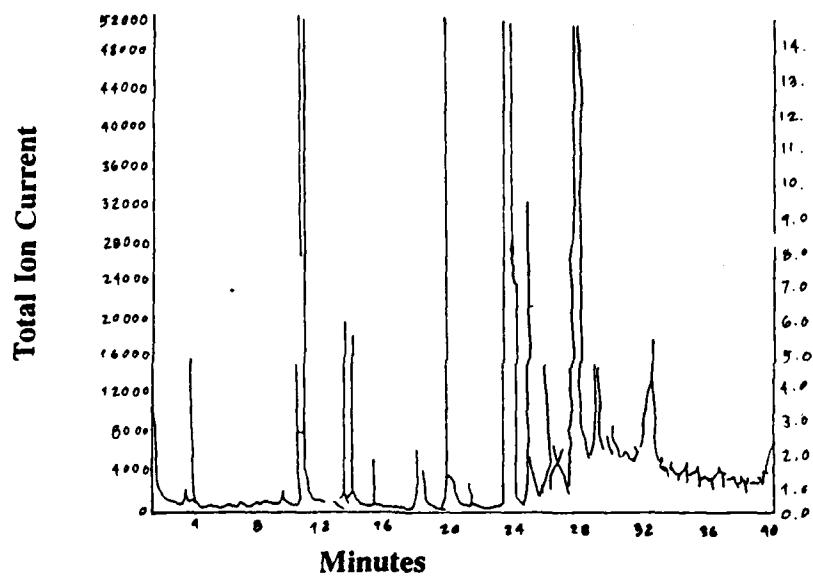
16c CO_2 Extraction Fraction 2
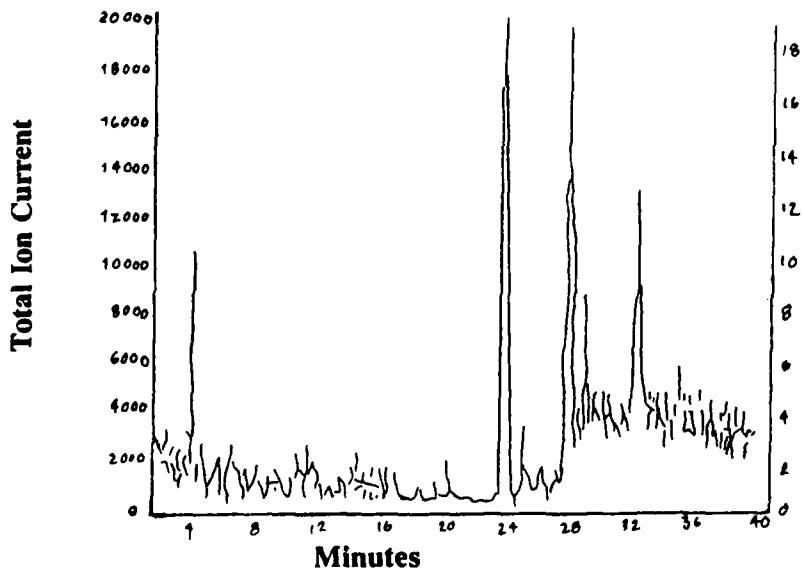
Figure 16.   Extraction of PECH (3M Dynamar Hx-102) with CO_2

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amu, which probably represents a cyclic tetramer.(18) It can be seen in Figure 8 that fraction 1 contains substantially all of the material eluting before 24 minutes as evidenced by the absence of this material in fraction 2. Both fractions show substantial peaks at 24 and 28 minutes. Peaks above 28 minutes are taken to be the beginning of the true polymer distribution.

d.   Extraction of PECH with Supercritical Propane

A sample of approximately 20.3g of PECH was extracted with supercritical propane at $120^{o}C$. The test is summarized in Table 22.

TABLE 22

3MPCH-2
Extraction of 3M PECH (Dynamar HX-102) with Supercritical Propane

$$T = 120^{o}C, Charge = 20.28g$$

Fraction	Max. Pressure (psig)	Standard Liters Solvent	Mass Collected (g)	w_i	Σw_i
1	1600	280	0.34	0.017	0.017
2	2800	520	0.71	0.035	0.052
3	4600	440	0.46	0.023	0.074
4	9000	1600	0.96	0.047	0.122

Chromatograms of the four fractions extracted with propane are shown in Figures 17a-d. It is clear from the chromatograms that substantially all of the material eluting at or below 28 minutes is eliminated in the first three fractions. This may be seen from the absence of these peaks in the chromatogram of the fourth fraction. It is important to note the change of scale in Figure 17d. (The small peak at approximately 12.5 minutes appearing in the fourth fraction is most likely an impurity since it does not appear in the parent material or the other chromatograms.)

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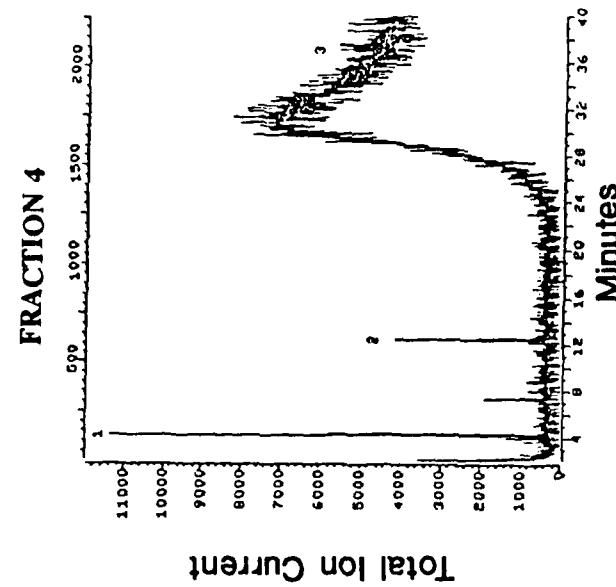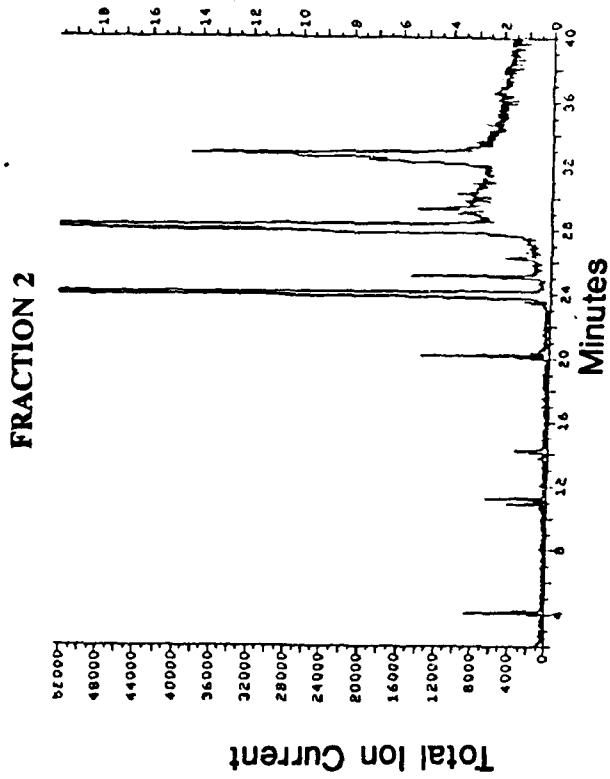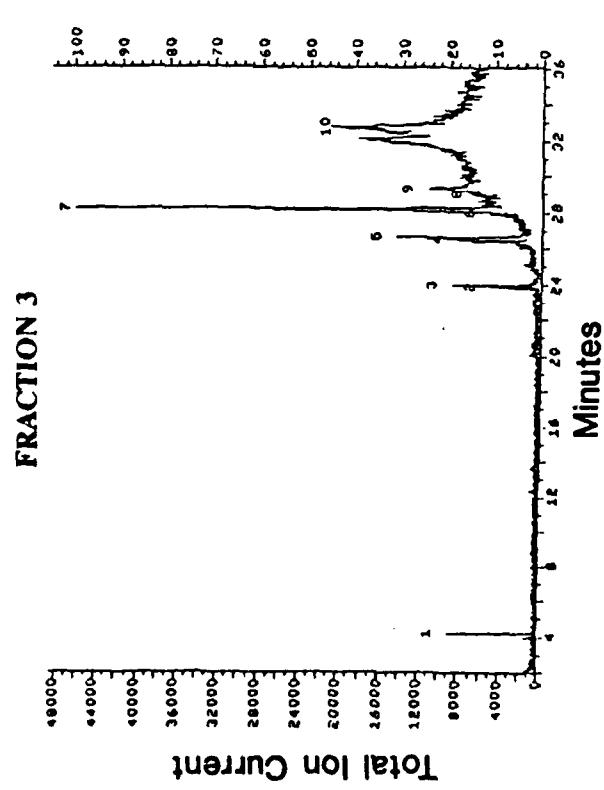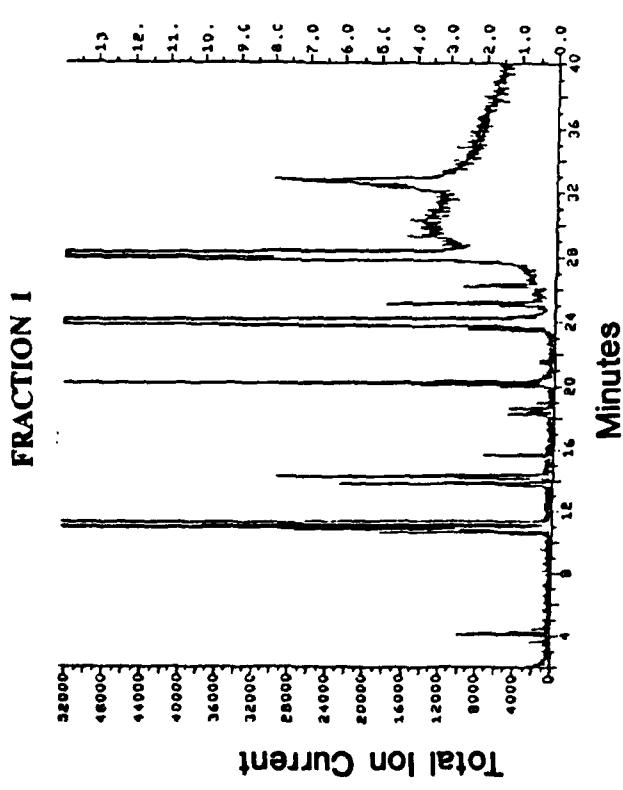
Figure 17.   Analysis of Fractions from (3M Dynamar Hx-102) with Supercritical Propane

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IV. EXTENSION OF SUPERCRITICAL FLUID EXTRACTION TO PRODUCTION SCALE

Operation of a supercritical fluid extraction process for the case of a solid feed was described in Section II. Recall in the process described that it was necessary during the course of the entire extraction sequence to stop (or divert) the gas flow, depressurize the extraction vessel, open the vessel, remove the residual solid material (which was chalk dust for the case described), refill the vessel with a new charge to be extracted, close the vessel, pressurize, and start the flow, the same sequence of operations also required for the separator section of the system where the product was recovered. It was briefly stated in the description that multiple extractors and separators in parallel would probably be more cost efficient for the batch solid extraction because much (or all) of the down time could be eliminated; with multiple vessels in parallel, for example, at the end of a cycle the gas flow could be diverted to another extraction vessel and separator that are piped in parallel with the vessels, of the first section system, and the emptying and filling steps could be carried out on "machine time". Each supercritical fluid extraction process application must be evaluated on a case-by-case basis to determine such design considerations; for example, for a small production volume, one extractor and one separator and one cycle per day may well be economic "enough" for that particular case, whereas with a much larger production rate, the multiple vessels layout may be more economic.

The design and process operation is greatly simplified in the case of a liquid feed and liquid extracts and raffinates. Figure 18 is a schematic diagram of a simple counter-current stripping process for a liquid feed. For purposes of providing a pictorial comparison to the process of Figure 2, the schematic diagram of Figure 2 is modified only in the addition of a continuous feed, a continuous draw off of raffinate, and a continuous draw off of extract from the separator: these streams are indicated by highly accented arrows in the figure. The internals of the extractor (and the extractor would be a small diameter pipe rather than the larger diameter vessel implied by the drawing) could be any type of area enhancement packing such as Raschig Rings, Berl saddles, wire mesh, etc., to promote good interphase mass transfer.

During the course of the Astronautics Laboratory program a number of extraction modes were investigated as described in Section III, one, simple stripping wherein only about 5 to 10% of the charge was extracted, and, another, a fractionation scheme wherein the charge was separated into X fractions of monotonically increasing molecular weight. (A multiple fraction separations process is discussed later in this section.)

The process for stripping low molecular weight components from propellant binders depicted in Figure 18 is an ideal one from both chemical engineering and supercritical fluids aspects. The (somewhat contrived) naphthalene - chalk dust separation discussed previously for its pedagogical value brought out the many separate steps required when a solid material must be extracted by a supercritical fluid. The "ideal" nature of the liquid process revolves around the facts that the polymer feed is a liquid, for example, both HTPB and GAP can be pumped continuously, the extract is a low molecular liquid and can be drained from the separator either continuously or intermittently via a pressure let down value, and the purified polymer devoid of its interfering components, but still a liquid stream, can also be drained continuously from the extractor via a pressure let down valve. This stripping system for HTPB is projected first for cost estimates.

PRESSURE
REDUCTION
VALVE

FEED →

EXTRACTION
VESSEL

SEPARATOR

COMPRESSOR

RAFFINATE
(Purified Polymer)
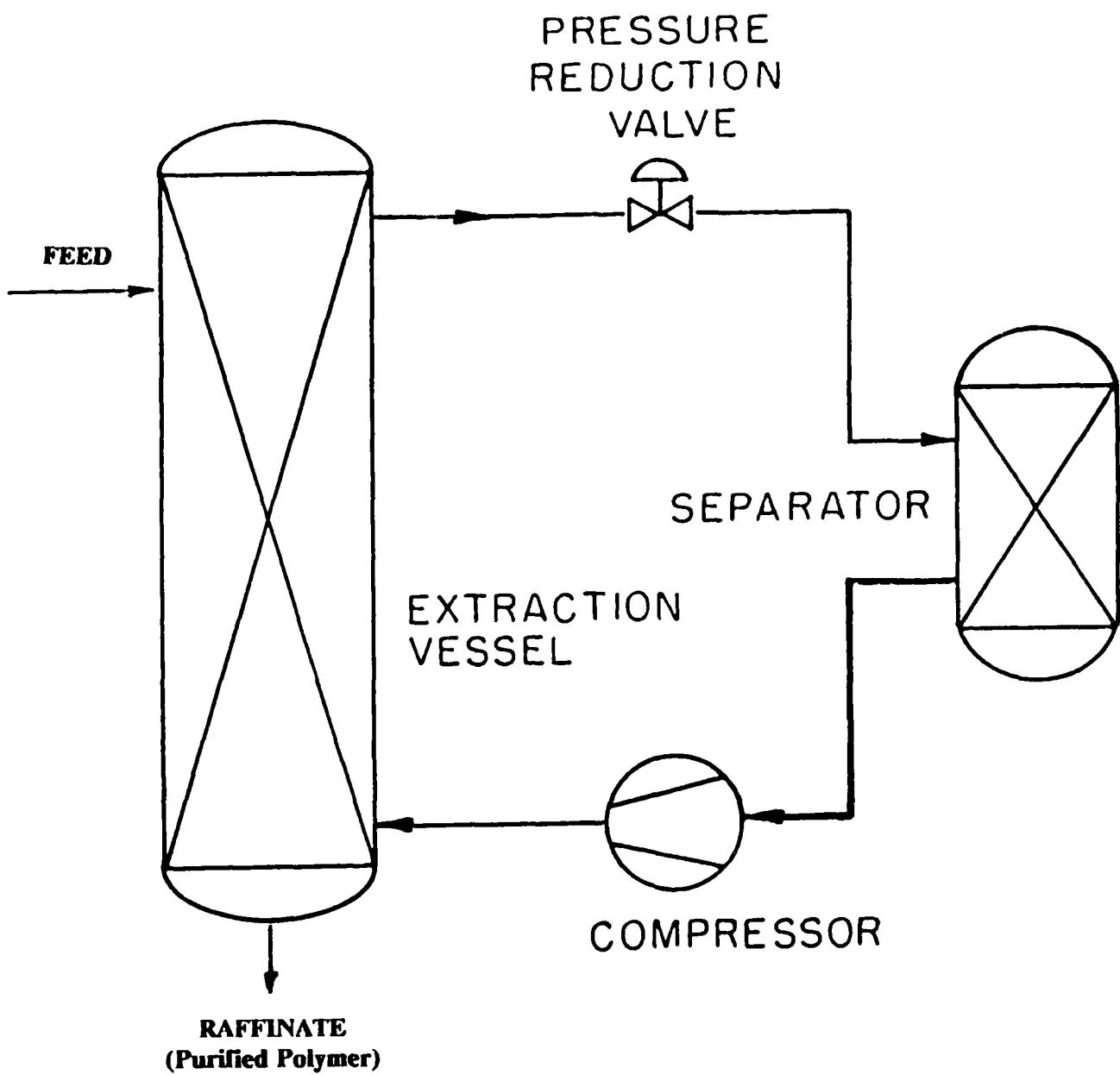
Figure 18.   Supercritical Fluid Extraction of HTPB

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A. Stripping of Low Molecular Weight Materials from HTPB - Cost Estimates

Preliminary estimates of the cost of processing HTPB and GAP polymer are developed below. Several yearly production levels have been designated by the Astronautics Laboratory Contract Monitor for economic evaluation, viz., 100,000 lbs/yr, 1,000,000 lbs/yr, and 10,000,000 lbs/yr. In all cases it is assumed that the plant is sized such that it operates continuously, i.e., at the chemical Process Industries standard of 330 days/yr. Even the 10,000,000 lbs/yr production level is small by Chemical Process Industries standards, i.e., it is equivalent to only 30,000 lbs/day. The 100,000 and 1,000,000 lbs/yr levels being much, much smaller will calculate to be quite costly, although on a positive note, here, the cost-benefit value of a supply of uniform propellant binder polymers in the missile and space programs has not yet been taken into consideration. It is, however, very tempting to extrapolate at this point of quite early development to the situation where one single multi-stage rocket is saved from performance or surveillance difficulties with the supply of an improved polymer binder and thus that the cost of processing is not the only factor to consider in the scale up.

The cost elements and calculations are outlined in detail; all figures are summarized in Table XXIII at the end of the cost elements and discussion. For each of the three production levels, the following considerations apply:

1. The Capital cost (installed cost) for the plant for simple extraction of low molecular weight species from HTPB
  a. 100,000 lbs/yr - $0.75 MM[*]
  b. 1,000,000 lbs/yr - $3.0 MM[**]
  c. 10,000,000 lbs/yr - $12.0 MM
The Capital cost contribution per lb of product for the respective production levels assuming a 5-yr, straight line depreciation schedule is, therefore,
  a. $0.75 MM/(5)(100,000) = $1.25/lb
  b. $3.0 MM/(5)(1,000,000) = $0.30/lb
  c. $12.0 MM/(5)(10,000,000) = $0.12/lb

2. Number of operating days, 330 days/yr

3. Salary plus fringe benefits, $150/person-shift; the number of persons/shift are a function of the production schedule. It is assumed that 2 persons/shift-day handle 100,000 lbs/yr; 3 persons/shift-day, 1,000,000 lbs/yr; and 8 persons/shift-day for 10,000,000 lbs/yr. Labor costs per lb of product are, thus,
  a. 100,000 lbs/yr - 2 x $150 x 3 x 330/100,000 = 2.97/lb
  b. 1,000,000 lbs/yr - 3 x $150 x 3 x 30/1,000,000 = $0.45/lb
  c. 10,000,000 lbs/yr - 8 x $150 x 3 x 330/10,000,000 = $0.12/lb

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[*]The $0.75 MM estimate for the 100,000 lbs/yr plant was determined from discussions with engineering firms and with vendors of equipment.

[**]Estimates for the larger plants were obtained from standard Chemical Process Industries extrapolation methods using the "0.6 rule", i.e., (size ratio)$^{0.6}$x cost of base.

As stated earlier the labor contribution to the cost of processing only 100,000 lbs/yr is quite large, and Phasex does not assume in its estimates a "0.37", or some other fractional and (mythical person) who can handle a 100,000 lbs/yr plant "full time". In its preliminary cost estimates Phasex errs on the high side, and, thus, rather high labor contributions to the cost have been calculated. As is also seen in the simple calculations and estimates given above, however, the labor costs decrease markedly with volume, to only $0.12/lb for a plant operating at 10,000,000 lbs/yr; this result, of course, derives from the economies of scale.

4. Supervision, accounting (e.g., of materials flow, transfer costs) and quality control will be assumed equal to labor costs as shown in item 3;
- a. 100,000 lbs, $2.97/lb
- b. 1,000,000 lbs, $0.45/lb
- c. 10,000,000 lbs, $0.12/lb

5. Buildings, facilities, will be assumed to be 25% of capital costs; the depreciation schedule for buildings is normally 10 or 20 yrs, but for simplicity and for reaching a very conservative estimate, i.e., to err on the high side, a 5 yr depreciation schedule is assumed. For the respective production levels the facilities costs are, then,
- a. $0.31/lb
- b. $0.08/lb
- c. $0.03/lb

6. Maintenance, 5% of installed capital cost/yr;
- a. $0.05(\$0.75 \text{ MM})/100,000 = \$0.38/lb$
- b. $0.05(\$3.0 \text{ MM})/1,000,000 = \$0.15/lb$
- c. $0.05(\$12.0 \text{ MM})/10,000,000 = \$0.06/lb$

7. Insurance, local taxes, 5% of capital plant cost plus buildings;
- a. $0.05(\$0.75 \text{ MM} \times 1.25)/100,000 = \$0.47/lb$
- b. $0.05(\$3.0 \text{ MM} \times 1.25)/1,000,000 = \$0.19/lb$
- c. $0.05(\$12.0 \text{ MM} \times 1.25)/10,000,000 = \$0.06/lb$

8. Gas make up, other supplies, utilities estimated at $0.20/lb independent of the production level; no attempt at, for example, optimized gas recovery, etc., has been factored in. Concerning gas recovery, some gas is dissolved in the polymer leaving the extractor. The gas can be largely recovered if the polymer is flashed to a lower pressure vessel, the gas that is released during depressurization collected, compressed and added to the recycle stream. (The bulk of the extraction gas stream being recirculated is, of course, recycled.) The dissolved gas recovery equipment consists of the flash vessel, associated pressure controls, and gas compressor. The amount of gas dissolved in the polymer at various combinations of pressure-temperature conditions was not measured on the program (nor was it considered important at this early stage); it is estimated that at 60°C, 1200 psi, the conditions at which one of the propane strippings was done, that the solubility of the gas in the polymer is only 10%, i.e., 0.1 lb propane/lb polymer leaves with the polymer. With propane at about $2.00/1000 Standard Cubic Feet, the propane loss is only 0.2 cents/lb polymer; thus the projected $0.20/lb makeup and utilities figure is probably very high (i.e., and no economic trade off between recovering the 0.1 lb/lb gas or flaring it was made).

9. Raw Materials Costs. In the case of stripping HTPB and GAP about 5-10% of the polymer was extracted. At a processing rate of 100,000 lbs/yr, this fraction will probably be discarded and is therefore will probably be discarded and is therefore a cost penalty; at a production level of 10,000,000 lbs/yr there may be a use found for the material. No raw material costs are considered for this estimate.

Certain Elements, e.g., labor costs, depreciation schedules, and similar factors may be different at different companies, but with all the factors enumerated above, however, the elements and contributions can be changed to suit the particular company's needs.

TABLE 23

Capital, Labor, and Other Costs for Supercritical Fluid Processing
of HTPB - Stripping of Low Molecular Weight Species

Plant Size lbs/yr Cost Component	100,000	1,000,000	10,000,000
Capital Cost, $/lb	$1.25	$0.30	$0.12
Labor costs, $/lb	2.97	0.45	0.12
Supervision, $/lb	2.97	0.45	0.12
Bldgs, facil., $/lb	0.31	0.08	0.03
Maintenance, $/lb	0.38	0.15	0.06
Ins., Taxes, $/lb	0.47	0.19	0.06
Gas, util., $/lb	0.20	0.20	0.20
Total fixed and oper. costs, $/lb	$8.55	$1.82	$0.71
Round up estimate	$9.00	$2.00	$1.00

B. Stripping of Low Molecular Weight Materials from GAP - Cost Estimates

A few operational differences exist between the HTPB and GAP stripping cases. With carbon dioxide as the stripping solvent the operating pressure level will be higher, 4000 psi instead of 1200 psi for the propane - HTPB case, the materials of contruction would be 316 stainless steal for all wetted parts of extractors, piping, etc., but no explosion proof electrical connections can eliminated for carbon dioxide (because, of course, carbon dioxide is not a flammable gas). As a general average first installed cost (non explosion proof) electrical runs about 10% of the total cost: for example, of $0.75MM total installed cost, electrical hook up would contribute about $75K. For explosion proof electrical wiring, actuator and transducer interfaces, controls, etc., the cost is about twice.

The current cost differential between carbon steel and stainless steel is about 2X and the difference in installed costs for the two materials is about 1.3. The installed cost of a stainless steel plant is not 2X times the cost of carbon steel because the material costs of piping, extractors, etc., contributes only about 35% of the total, and, the electrical hook up of a stainless steel control valve, for example, is exactly the same as for a carbon steel valve, the hook up of a motor driving a carbon steel pump is the same as for a stainless steel pump, and similar considerations).

Since the operating pressure for GAP extraction with carbon dioxide is higher than for propane extraction of HTPB, the vessels and piping will cost more, not just because stainless steel is the material of construction but because the vessels and piping must operate at higher pressure thus requiring thicker walls, higher pressure fittings, etc. Based upon experience of a plant design and construction company and discussions with them, it is estimated that a differential cost for the GAP stripping plant is about 40%, e.g., the cost for the 100,000 lbs/yr GAP plant would be $1.05 MM.

The individual cost contributions for the plant will be analogous to the factors outlined in Items 1-9 above and are calculated the same way; cost factors are summarized in Table 24.

TABLE 24

Capital, Labor, and Other Costs for Supercritical Fluid Processing of GAP - Stripping of Low Molecular Weight Species

Plant Size lbs/yr Cost Component	100,000	1,000,000	10,000,000
Capital Cost, $/lb	$1.75	$0.42	$0.17
Labor costs, $/lb	2.97	0.45	0.12
Supervision, $/lb	2.97	0.45	0.12
Bldgs, facil., $/lb	0.44	0.11	0.04
Maintenance, $/lb	0.53	0.21	0.09
Ins., Taxes, $/lb	0.66	0.27	0.09
Gas, util., $/lb	0.20	0.20	0.20
Total fixed and oper. costs, $/lb	$9.52	$2.11	$0.83
Round up estimate	$10.00	$3.00	$1.00

C. Complete Fractionation of HTPB and GAP

In addition to estimating the costs of the stripping of low molecular weight species from HTPB and GAP, the Astronautics Laboratory Contract Monitor also stipulated that the costs of completely fractionating, both polymers be estimated; a three fraction scheme was desired. The generic process for fractionating a polymer was described in Section II.

Relative to the process shown in Section II, to obtain three fractions only three vessels are required. In the process polymer is pumped to the first vessel where about 10% of the polymer is obtained as a high molecular weight raffinate, a first pressure reduction step promoting precipitation of about 80% of the original feed in vessel 2, and a second pressure reduction causing the remaining 10% to precipitate in vessel 3, the gas from the third vessel recycled by the compressor to the initial vessel.

For the degree of accuracy that is required for this preliminary economic evaluation the final costs for both HTPB and GAP fractionation will be assumed to be about the same as for the stripping process of GAP, but the products obtained from the fractionation are, of course, quite different. Recall also in keeping with Phasex practice the higher costs (for GAP) are assumed here and are summary in Table XXV.

As discussed in Section III Table XXV here, chlorodifluoromethane exhibited the ability to fractionate GAP. Chlorodifluoromethane is a hydrogen-containing chlorofluorocarbon, i.e., it is an HCFC rather than a CFC, the latter class of compounds being phased out of usage by the year 2000 by the Montreal Protocol. The HCFCs are much less an ozone depletion problem and accordingly will probably not be phased out until 2040. Thus, the work carried out on the fractionation of GAP has long range potential viability especially in light of the fact that GAP itself is still undergoing extensive testing in various industrial and government laboratories. Additionally on the Phase I program an extensive evaluation of all supercritical fluids was not carried out so there may well be other simple gases that can fractionate GAP. Such an evaluation is later recommended to be done in a Phase II study.

TABLE 25

Bottom Line Cost for Fractionating HTPB and GAP

Plant size, lbs/yr	100,000	1,000,000	10,000,000
Round up estimate	$10	$3	$1

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V. CONCLUSIONS AND RECOMMENDATIONS

The feasibility of fractionating prepropellant binders, specifically HTPB and GAP, has been demonstrated using supercritical fluid solvents. The process is readily scaleable to produce large quantities for performance test and field evaluation. It is estimated that production level quantities, e.g., 1,000,000 lbs/yr and 10,000,000 lbs/yr, binders with uniform and improved performance characteristics be produced economically at a cost of $3/lb and $1/lb respectively.

Fractionation and analysis of sufficient quantity of prepropellant polymer for use in formulation and casting tests of each fraction would, for the first time, provide the means for directly evaluating the effect of molecular weight, functionality, presence/absence of impurities, and other factors affected by the fractionation on performance. These tests should result in the identification of the optimum fractions and those fractions and components responsible for performance problems.

On a somewhat smaller scale and not addressed in the Experimental section, high quality GPC standards may be produced via SCF fractionation. At present the HTPB standards, when available, are of very poor quality (19). The availability of high quality standards would benefit the government and contractor labs involved in propellant characterization.

The next step toward evaluating SCF fractionation of propellant binders as a production scale process is the extension of the laboratory work contained in this report to pilot scale operation. The pilot plant extractions would be operated in a counter-current continuous manner which is typical of a production facility, and the samples generated from the pilot work could be used in the performance test mentioned above.

The success of the feasibility tests indicate the potential for future work in both the analytical and production areas, and funding of a Phase II effort is clearly warranted based upon the successful experimental results and the attractive economics which were projected based upon the experimental work.

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